FURTHER STUDIES ON CATALYTIC DECOMPOSITIONS OF PHENOL SALTS

A Thesis

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by
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Introduction.

Work has been in progress for some time in these laboratories on the decompositions of the silver salts of symmetrically trihalogenated phenols.[1] It has been shown that these salts can be decomposed in two ways. In each case silver halide is split out leaving an unsaturated residue, as expressed by the following equation:

$$C_6H_2X_3OAg \text{ --- } C_6H_2X_2O + AgX$$

This decomposition can be brought about catalytically in cold undiluted ethyl iodide and other similar solvents, the change being usually accompanied by the production of a brilliant blue or green color which soon fades. The decomposition can also be brought about by boiling the salt for a short time in benzene, the color usually not being so noticable but the reaction products being apparently identical.

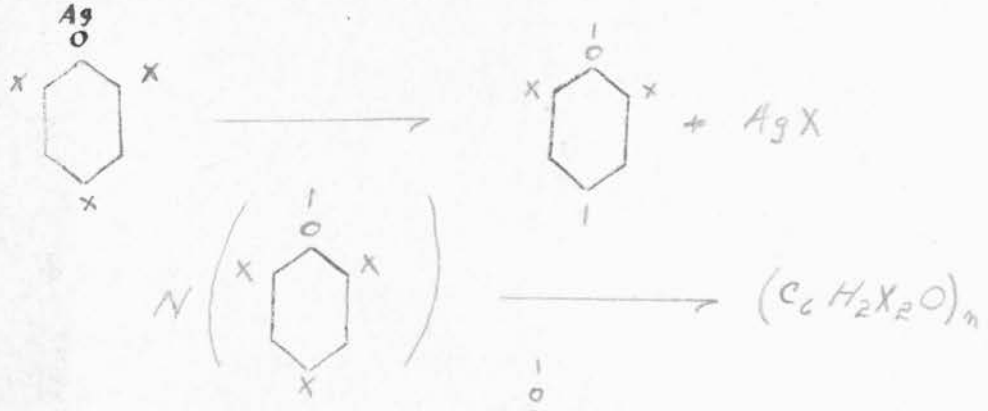
The products other than silver halide were found to be colorless amorphous substances of high molecular weight, i.e. polymers of the residue left after abstracting silver halide from the original salt. They have been given the general formula $(C_6H_2X_2O)_n$.

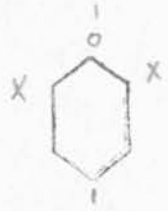
In recent work in which he used phenols containing different kinds of halogen in the same ring, Joyce[2] has shown that either para or ortho halogen may be split out. No definite rule could be devised for the relative reactivity of the halogen in the two positions as the preference seems to depend not only on the position but on the nature of the halogen; its affinity for silver and the benzene ring. The evidence seems to point to the para position

1. J.A.C.S. XXXVIII, 1761, 1916
2. Master's thesis, unpublished.

as the preferred one when only one kind of halogen is present.

The reaction is considered to be intramolecular and the following mechanism has been suggested:



The substance  has already been spoken of as an unsaturated residue. It is believed that it is actually present in the solution for a short time, polymerizing rapidly to form the amorphous compounds.

In view of the work of Joyce it is well to point out that the unsaturated residue may also have the formula 

Under the proper conditions it has been found possible to get from the silver salt of s-tri-iodo-phenol[1] by catalytic means either a white amorphous oxide or a deep red amorphous substance of identical composition. This red substance has been known for some time under various names. Until the author's view of it is developed it will be spoken of as "Lautemann's Red".[2]

The work in this thesis may best be considered under four heads:

First, the structure of the "Red" substance.

Second, the mechanism of the reaction by which it is produced.

Third, the relation between the "Red" and the white amorphous

1. J:A.C.S.XXXVIII, 2474,1916
2. Ann. 120, 309. 1861

compounds.

Fourth, an investigation of other reactions by which unsaturated residues may be produced which might lead to the formation of similar amorphous oxides.

The work thus outlined has been accomplished both by analyses of the "Red" and by a study of the number of new reactions which lead to the formation of the white or "Red" oxides.

More reactions have been found to yield the colorless oxides than colored ones. Some of them may be looked upon as oxidations of the various phenols. One method may be considered a reduction of tri-bromo-phenol bromide.

The literature of the past fifty-six years contains many articles on the oxidation of substituted phenols. These oxidations have led chiefly to three different sorts of products, mono-nuclear quinones, di-nuclear quinones, and amorphous bodies about whose structure considerable confusion still exists.

The products obtained depend upon the number and nature of the substituents, their position relative to the hydroxyl group and the conditions prevailing during oxidation.

No connection seems to have been assumed so far, to exist between the conditions which lead to these three different kinds of oxidation products.

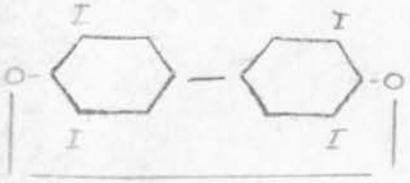
Pummerer and Frankfurter[1] have mentioned that these three kinds of products are obtained but attempt no explanation.

The earliest mention of one of these products, which is also the one in which we are most interested is by Lautemann[2] in 1861,

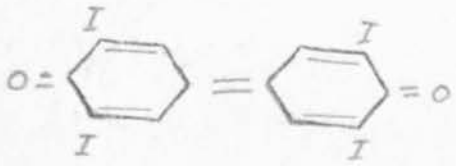
1. Ber. 47, 1472, 1914
2. Loc. Ct.

who by boiling salicylic acid with alkali and iodine obtained a deep purple-red powder, insoluble in all ordinary solvents except carbon disulphide. He called the substance di-iodo-phenylene oxide  , as its analysis corresponded to that formula.

Kammerer and Benzinger[1] in 1878 also worked with this compound. Their most important contribution was a new method of preparation, by treating phenol in sodium carbonate solution with K I_3 solution at the boiling temperature. From their work they concluded that the substance was crystalline and had a structure indicated by their name for it, tetra-iodo-diphenylene quinone.



or



We propose to show that both Lautemann's and Kammer and Benzinger's formulae are wrong, and that the substance belongs to the third class of oxidation products, ie. the amorphous ones.

Magatti[2] and Bogault[3] accepted Kammerer and Benzinger's findings without investigation. Kekule[4] was more cautious and said: if the formula assigned to this substance was correct, we were dealing with a case of the direct substitution of iodine in

1. Ber. 11, 557, 1878
2. B. 13, 226
3. J.C.S. abs. II. 738, 1906.

the benzene ring.

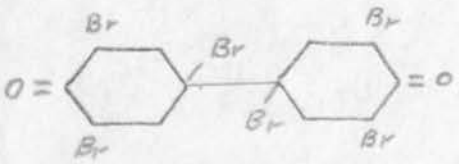
Messinger and Vortmann[1] called it di-iodo-phenyl hypoidite

also erroneously.

Thus we see that tho this "Red" has been known for quite a long time no agreement has yet been reached concerning its structure. All agree, however, that it is an inert purple substance, very insoluble except in CS_2 and that it is made by action of iodine on phenol in alkaline solution.

A white substance containing bromine of composition analogous to the "Red" was obtained by Kastle[2] by the decomposition of tri-bromo-phenol bromide by sunlight in CS_2 solution. He gave the di-nuclear formula $(C_6H_2Br_2O)_2$ but the substance seems to be identical with the oxide derived from the silver salt of tri-bromo-phenol.

A similar substance had been obtained by Benedikt[3] and others from the decomposition of tri-bromo-phenol bromide by heat in carbon dioxide. This substance has nearly the same physical properties as the above oxide but contains one atom of bromine more per benzene ring, and was thought by Benedikt to be -hexa-bromo-dipheno quinone.



1. Ber. 23, 2753, 1890.
2. J.A.C.S. 27, 31, 1902.
3. Ann. 199,134, 1879. Olivier, R. 28, 354 (C1910 I 571)

S.C.J. Olivier[1] studied this compound and found its molecular weight high, giving it the formula $(C_6H_2Br_3O)_n$. It will at once be noticed that this corresponds in form to the formula already given to the white oxides from our silver salts. Kastle[2] claims to have made this substance also, by the action of tri-bromo-phenol silver salt on tri-bromo-phenol bromide. This work has been repeated by us and will be discussed later.

A tetra-chlor-phenylene oxide is described by Merz and Weith[3] as made by distillation of penta-chloro-phenol potassium salt. It is a crystalline substance of definite melting point (320°). It has also been described by Hugounenq[4] and has been given the formulae: C_6Cl_4O ,

A phenylene oxide has been described by Märker[5], who made it by distillation of salicylosalicylic acid. It is given the formula C_6H_4O and is crystalline.

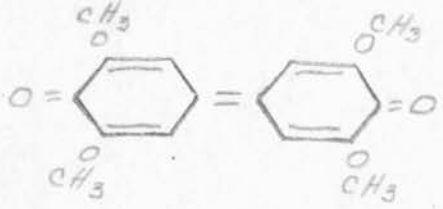
A diphenylene-dioxide[6] was made by heating ortho-chloro-phenol alkali salts.

These last three substances are all colorless and crystalline and have definite melting points thus differentiating them from the amorphous oxides and the colored quinoid products.

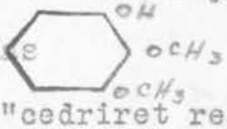
1. Loc. Cit.
2. Loc. Cit.
3. B. 5, 461.
4. A.Ch. (6),20,546.
5. A. 124, 249,1862.
6. D.R.P.223, 367, 1909.

It is remarkable how persistently the different authors have mistaken these amorphous substances, both colored and colorless, for di-nuclear quinones. This tendency probably arises from the fact that just previous to Kammerer and Benzinger's[1] work A.W.Hofmann[2] had obtained cedriret or corrulignone by the oxidation of s-pyrogallol di-methyl ether.

Cedriret had been shown by Liebermann[3] to be a true di-nuclear quinone, tetra-methoxy diphenylene quinone,



This coupling of two nuclei is one of the most interesting of the oxidation reactions and has been found to occur in other instances.

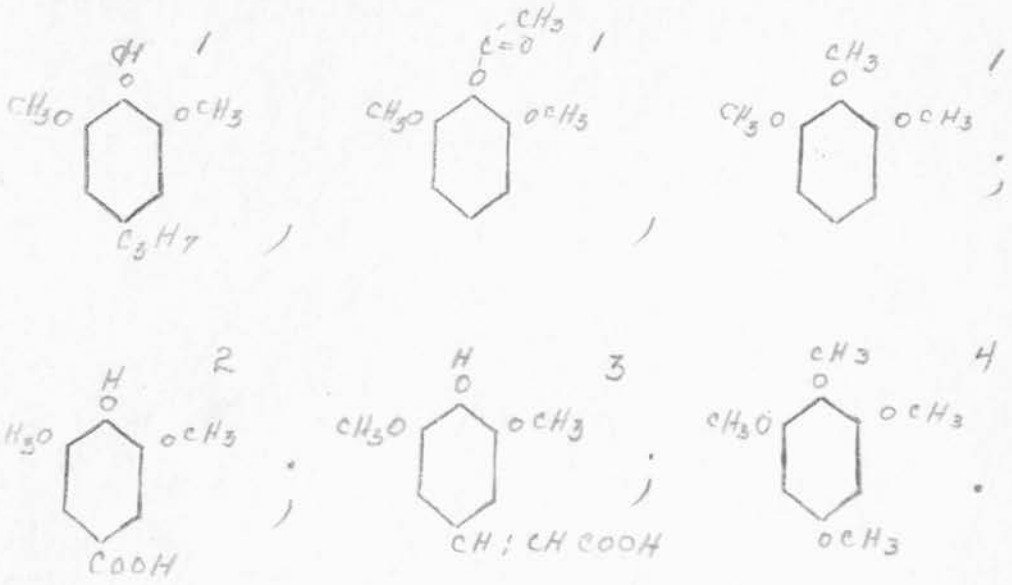
Anwers and Markovitz[4] found that vicinal meta xylenol gave this reaction while pseudo cumenol, mesitol, and the other xylenols did not. The other pyrogallol dimethyl ether has  has been shown by Herzig and Pollak[5] not to give the "cedriret reaction".

The methylene[6] ether also did not give it.

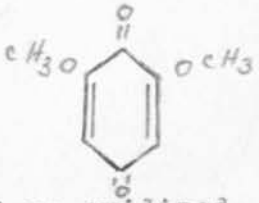
Hofmann[7] concluded that the tendency to form a coerulignone type of compound was lost when the H of the hydroxyl or the one para to it in his ether was replaced. This is borne out by the

1. B. 11, 557, 1878
2. B. 11, 333,1878
3. Ann. 169, 221,1873
4. B. 38, 226, 1905
5. M. 25, 501, 1904
6. Magatti, B. 12, 1863 (1879)
7. Loc. Cit.

action of the following compounds:

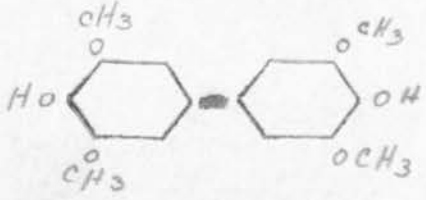


1. B. 21, 602, 2020, ©1888
2. B. 38, 226, 1905
3. B. 30, 2333, 1897
4. B. 21, 610, 1888

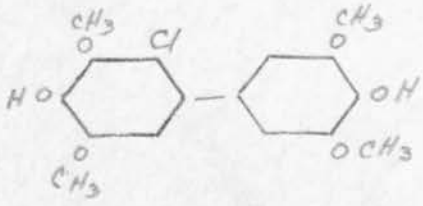


All of these give the mono nuclear quinone

The corrulignones can be easily reduced and re-oxidized, halogen in the nucleus interferes with re-oxidation as shown by Liebermann[1] who upon chlorinating hydro-corrulignone



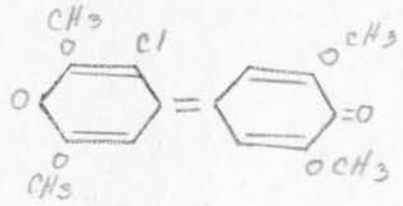
got a monochlor derivative



which he could not easily oxidize to the corresponding chloro-

1. B. 31, 618, 1898.

corulignone



while without the chlorine the oxidation proceeded smoothly.

Oxidations of the tetra-bromo-diphenol[1] and tetra-chloro-diphenol and of diphenol[2] itself have been accomplished yielding cedriret types but in these cases the molecule was of course not doubled by the reaction.

The first two of these are the true bromine and chlorine analogues of the compound Kammerer and Benzinger thought they had prepared.

1. Magatti, B. 13, 226, 1880. Bayer Ann. 202, 122,(1880)

THEORETICAL PART

"Lautemann's Red"

An investigation of the so-called Lautemann's Red has been steadily becoming of more importance in connection with our work on the decomposition of halogenated phenol silver salts. The substance was of interest both because of its composition which is exactly analagous to that of the poly-di-brom-phenylene oxide[1], and because of its probably difference in structure as indicated by its color.

The first discovery, that either a white poly-di-iodo-phenylene oxide strictly analogous to the brominated oxide, or a red one (Lautemann's Red) could be obtained from the silver salt of S-tri-iodo-phenol[2] made a complete investigation of the "Red" of the greatest importance.

The points to be settled were, the structure of the "Red", its relation to the white oxides and the mechanism of the reactions by which they are produced.

A clue to the last question was obtained from a more or less accidental occurence.

In preparing the silver salt of tri-iodo-phenol, a solution was used which contained just enough alkali (KOH) to keep the phenol dissolved. This was obtained by first dissolving the tri-iodo-phenol in excess of potassium hydroxide and adding acetic acid till a faint precipitate formed. This was filtered off leaving the solution of"neutral" potassium salt which of course was always

1. J.A.C.S. 38, 1761, 1916.
2. J.A.C.S. 38, 2474, 1916.

alkaline to litmus. The silver salt was ordinarily precipitated by adding silver nitrate to this solution.

Solutions of this "neutral" potassium salt had a very troublesome tendency to decompose, especially while being filtered by suction. Decomposition was denoted by the appearance of a voluminous deep purple precipitate, which proved to be "Lautemann's Red" "LAUTEMANN'S RED".

Solutions containing excess alkali did not have this tendency. Obviously some agent whose activity could be destroyed by alkali caused the decomposition. As the phenomenon appeared most often during filtration by suction, the air of the laboratory was suspected of containing the active agent.

Bromination had been carried out in the laboratory previously, altho no appreciable amount of bromine was present at the time.

Solutions of "neutral" potassium salt were exposed to extremely small quantities of bromine vapor whereupon they were found to begin to decompose immediately. The decomposition rapidly proceeded to completeness. Other halogens produced the same effect, the extremely small qnantity necessary showing the action to be catalytic. Excess alkali was found to prevent the change also, as would be expected.

The pure potassium salt was isolated in order to exclude all other possible factors in the change. The pure salt was found to give the characteristic reaction when wet; bromine, iodine, sunlight, and heat were each found to be capable of causing the change.

In the case of sunlight, and catalytic amounts of bromine the decomposition was shown to go practically to completion as 94-98 °/° of the theoretical amount of "Red" was obtained.

One point of similarity between the production of the white oxides and the "Red" is thus established, they may both be produced by catalytic reactions, though of very different kinds.

A description of the potassium salt may find place here.

Two forms were prepared, one anhydrous and the other containing one molecule of alcohol. Both varieties are yellow. The intensity of color is decreased on strong cooling and increased on heating. In each case the color returns to the original on return to normal temperature. The anhydrous salt on crystallizing from a mixture of benzene and alcohol which was cooled by evaporating in vacuo, came out nearly white but soon acquired the characteristic yellow tint.

Great care was taken in preparing pure salt from pure tri-iodo phenol in order to test the color, but the purest samples obtained were not noticeably less yellow. The idea of oxidation as a cause of the color was also considered, but discounted as the increase of color caused by heating is lost on cooling. Further, no increase in color is noticed in the pure salt on long standing.

The potassium salt of tri-bromo-guaiacol[1] is yellow and of about the same shade and may suggest the quinoid structure for part of our potassium salt.

The salt is very unstable as shown by its ready decomposition, especially in the presence of moisture. The "Red" is not given by the decomposition of the dry salt either by heat or by the catalytic agents mentioned. Instead the salt is "charred".

1. J.A.C.S. XXXIII, 201, 1911.

The potassium salt of tri-bromo-phenol, which is white, can be decomposed either thermally or catalytically. The catalytic decomposition takes place with far less readiness than with the corresponding tri-iodo compound.

The result of thermal decomposition either dry or in benzene is a white amorphous substance containing 64.0% bromine. It is a poly-di-bromo-pehnylene exide apparently identical with the one from the silver salt.

The result of catalytic decomposition of water solutions of the tri-bromo salt by iodine is an amorphous substance of similar properties to the others but of a deep orange color. Analysis shows the bromine content to be about 1/2 o/o lower than that of the white.

This is the bromine analogue of "Lautemann's Red", with considerable"white"mixed with it, as it can be separated into fractions of different depths of color. It was the fraction of deepest color which was analyzed and gave the low result.

The point to be emphasized here is that this orange colored substance is not the crystalline tetra-bromo-di-phenylene quinone which we have made and compared directly nor is it a mixture or adsorbtion compound of that and the white oxide, for all attempts to prepare adsorbed mixtures from those two substances were failures.

The true tetra-bromo-di-phenylene quinone was made from tetra-bromo-diphenol, by the method of Magatti.[1] It showed a remarkably beautiful crystalline structure. The color was a deep orange-red by transmitted light and red-violet by reflected. It was also found to be sparingly soluble in benzene, carbon disulphide,etc. and not in-soluble in alcohol. All solutions, however, showed an orange color

1. Ber. 13, 227

All its properties were entirely different from those of "Lautemann's Red" or the orange amorphous substance from the tri-bromo-phenol.

"Lautemann's Red" has been assigned an analogous structure, but this must now be modified in view of the observation mentioned, and those to be given below.

The "Reds" made from the potassium salt of tri-iodo-phenol a and by Kammerer and Benzinger's method do not differ from each other more than samples of each method differ among themselves. Analyses for iodine by Lautemann, Kammerer and Benzinger and by us, all agree very well and they also agree with the various formulae proposed for the substance. Analysis therefore is of no value here beyond excluding non-isomeric substances.

Five structural possibilities may now be considered:

I. The di-iodo-phenylene oxide of Lautemann.

II. The tetra-iodo-diphenylene quinone of Kammerer and Benzinger.

III. A substance strictly analogous to the white poly-di-bromo-phenylene oxide.

IV. A mixture of two or more of these substances.

V. A substance differing from all of them.

The first structure is conceded in the literature to be wrong and is eliminated with some of the others by facts given below, especially determinations of molecular weight.

The second has little to support it. The "Red" is colored and can be reduced easily to a colorless substance which in turn

can be re-oxidized to a colored substance like the original. This indicates a quinoid structure, but the reduction product is not soluble in alkali as would be expected of tetra-iodo-diphenol. Further, neither the "Red" nor its reduction product could be made to crystallize. Therefore the reduction product cannot be tetra-iodo-diphenol.

The best test is the oxidizing power of the "Red" which is far below that required by Kammerer and Benzinger's formula.

They base their formula on determinations of this oxidizing power shown toward sodium sulphite but were unable to duplicate the determinations which coincided with their theory.

Our method of determining the quinoid oxygen consisted in measuring the volume of nitrogen set free from hydrazine by a known weight of the "Red". The values varied considerably as shown by the table on page 21 . The extreme values are .95 o/o and .36 o/o of quinoid oxygen both far below the 4.65 o/o which would be present in tetra-iodo-diphenylene quinone.

This method of determining quinoid oxygen gave excellent results when used on tetra-bromo-diphenylene quinone and cedriret, as can be seen by referring to the table. It should give equally good results with the iodine analogue of these.

The variations in the per cent quinoid oxygen as well as the reaction by which it is calculated, will be discussed later. Enough only is given here to exclude Kammerer and Benzinger's hypotheses.

Added to these considerations are the molecular weight determinations which were found cryoscopically in bromoform and

ethylene dibromide and were found to vary between about 2300 and 4800. This excludes both Lautemann's and Kammerer and Benzinger's formulae.

These weights are of course low rather than high as the substance is amorphous and therefore hard to purify and as almost any impurity would have a smaller molecular weight than the "Red", thus bringing down the average. These values can only indicate the order of molecular magnitude. The molecular weight of tetra-iodo-diphenylene quinone is 688.

The third possibility, that of its being an analogue of the poly-dibromo-phenylene oxide, which might be colored on account of its iodine content, fails, as the white iodine analogue of this has been made from the silver salt of tri-iodo-phenol[1] by methods strictly analogous to those used in preparing the corresponding bromine compound. This white iodine containing oxide differs from the "Red" in color, it is also different from the colorless reduction product of the "Red" as it cannot be oxidized to a "Red" by agents which do reoxidize the reduction product of the "Red".

The fourth possibility, that of a mixture or adsorbtion compound of two or more of the above substances, is rendered improbable by the following observations.

Between the white oxide from tri-bromo-phenol and the true tetra-bromo-diphenylene quinone there is a great difference in solubility. Such a difference should exist between the corresponding iodine derivatives, yet no evidence of separation, by fractional precipitation, into fractions of even moderately differing properties has been observed with the "Red", in investigating this possibility.

The true tetra-bromo-diphenylene quinone and the poly-dibromo-phenylene oxide have been thrown out of solution together, the white

1. Loc. Cit.

has also been precipitated in a solution of the quinone without showing the slightest tendency for the two to separate together. If strong adsorbtion took place with the iodine compounds it would also be expected some similar tendencies would be shown by the bromine analogues.

Tetra-bromo-diphenylene quinone is but sparingly soluble in carbon disulphide while the "Red" is extremely soluble, showing it could not contain a large amount of an iodine analogue of the tetra-bromo-diphenylene quinone. Further, "Red" recovered from filtrates, i.e., the most soluble fraction was found not to differ materially in oxidizing power from the other samples of "Red".

Lastly, it would be expected that some of the hydroquinone could be extracted by alkali from the reduction product of the "Red" if it were a mixture and even if it were an adsorbtion compound. This could not be done.

This leaves only the fifth possibility,-- the "Red" is something different from all of these. However, it is a substance with some properties belonging to both the hypothetical tetra-iodo-diphenylene quinone and the poly-diiodo-phenylene oxide. It is a quinoid substance of high molecular weight.

A consideration of the tables on pages 18 and 21 will throw some light on the structure of the "Red". Analysis shows it to have the empirical formula $C_6H_2I_2O$, molecular weights show this must be modified to $(C_6H_2I_2O)_n$. It can be reduced to a colorless substance which differs very little in composition, indicating with the high molecular weight that not all of the oxygen is reducible.

Analyses

Substance	Weight grams	Weight Ag I	o/o I found	Formula	o/o I Calculated
Original	.1407	.1915	73.54	$(C_6H_2I_2O)_n$	73.82
"Red" A	.1085	.1471	73.25		
Reduced "Red"B	.1364	.1849	73.24	?	?
Acetylated	.1169	.1562	72.19	$(C_6H_2I_2O\text{-}1/5CH_3CO)_n$	72.02
"Red" C	.1147	.1526	71.88		
Hydrolyzed Red D	.1422	.1928	73.25	?	?
Regenerated RedE	.1335	.1827	73.93		
" " " "	.1321	.1795	73.42	$(C_6H_2I_2O)_n$	73.82
Insoluble Red	.1101	.1476	72.43	$(C_6H_2I_2O)_n$	73.82
Red	.1200	.1635	73.62	$(C_6H_2I_2O)_n$	73.82
from K salt	.1658	.2246	73.20		

Molecular Weights

Substance	Weight gram	Solvent	Weight Solvent	Δ	Molecular Weight
"Red" by Alcohol	.2428	$CHBr_3$	100 g.	.015°	2330
	.8131	"	"	.050°	2330
	.6386	"	"	.029°	3140
Original "Red"A	.5342	$C_2H_4Br_2$	50 g.	.026°	4850
Reduced "Red" B	.5578	"	"	.029°	4540
" " "	1.0653	"	"	.051°	4950
Acetylated "Red"C	.5075	"	"	.026°	4610
" " "	1.0172	"	"	.058°	4760
Hydrolyzed "Red"D	.5062	"	"	.022°	5430
Regenerated"Red"E	.5232	"	"	.022°	5510
" " "	1.0302	"	"	.038°	6390
" " "	.5258	"	"	.015°	8470
Red from K salt	1.0741	$CH Br_3$	100 g.	.055°	2810
Red reduced	.5122	$C_2H_4Br_2$	50 g.	.035°	3440
by HI	.7242	"	"	.036°	4750
same Re-oxidized	.5587	"	"	.032°	4120

A change from $C_{12}H_4I_4O_2$ to $C_{12}H_6I_4O_2$ calls for a drop in iodine content of about .2 o/o. Too much stress cannot be laid on this as the substance is amorphous and hard to purify and the analyses are slightly low.

More reliable results may be obtained from the acetyl derivative of the reduction product. Analyses of this substance show a slight but unmistakeable drop in iodine content corresponding nearly to that required by the addition of one acetyl group to every five $C_6H_2I_2O$ groups, though of course it does not seem wise to use the latter figures as exact.

This acetyl derivative has not suffered any other change than acetylation as it can be hydrolyzed and re-oxidized to a "Red" like the original both in appearance and analysis. Oxidation would not work before hydrolysis showing that we were dealing with a true acetyl derivative.

As the hydrolysis is somewhat difficult and the amount of acetic acid liberated very small it could not be determined with any accuracy.

Vigorous reduction by hydriodic acid reduced the iodine content somewhat, as was to be expected. The new iodine content remained practically constant on oxidizing this reduction product to a "Red" showing the change to the quinoid group was reversible.

The molecular weight determinations show three things:

I. The molecular weight is high and variable.

II. The weights taken in bromoform are uniformly lower than those in ethylene dibromide. Bromoform as a solvent was discarded, not because of this but because of its instability. This must be kept in mind when interpreting results, tho even if the weights in bromoform are taken to be correct it in no way interferes with our conclusions.

III. The molecular weight gradually rises on continued manipulation as shown by the rise stepwise from 4800 to 8000 by taking the sample through four processes, reduction, acetylation, hydrolysis, and re-oxidation.

This may be due to two causes:

First, by further polymerization which is not only possible but quite probable.

Second, by gradual loss of molecules of like structure but lower molecular weight than the average. This also seems to us to be likely as will be shown.

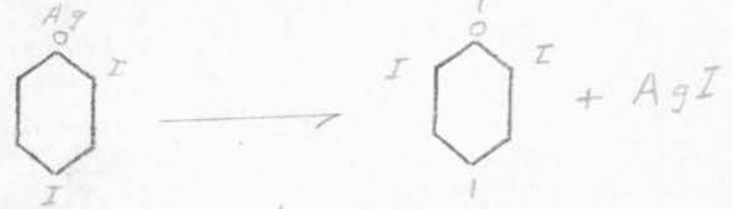
An examination of the table showing the percentage of quinoid oxygen, page 21 , shows that while this varies somewhat it is very low and is related to the molecular weight in that as one increases the other decreases. On the average about 12 o/o of the oxygen appears to be quinoid.

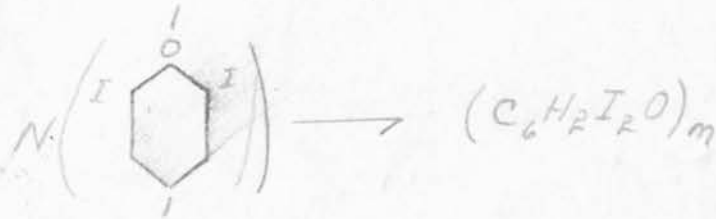
Determination of Quinoid Oxygen.

Sample	Substance	Weight g.	T.	P.	N_2 c.c.	o/o Quinoid O	o/o Quinoid O	o/o Calc
	Tetra-bromo	.5034	32	738	13.8	6.57		6.40
	dipheno quinone	.4700	32	738	12.55	6.42		"
	Cedriret	.1752	32	746	7.6	10.57		10.53
I	"Red" from CS_2	1.3240	33	741	4.1	0.75	0.38	
I	" " "	.7365	30.5	740	2.5	0.81	0.41	
II	" " "	.9790	33	740	3.9	0.95	0.48	
II	" " "	.9130	31	740	3.5	0.91	0.46	
III	" " "	.579	28	742	1.0	0.41	0.21	
IV	" " "	.613	28.5	734	1.0	0.39	0.20	
V.	" " "	.768	30	740	1.5	0.47	0.24	
I	"Red" by Alc.	.593	30	740	0.9	0.36	0.18	
II	" " "	.925	28	742	1.6	0.40	0.20	
III	" " "	.663	28	740	2.1	0.75	0.38	
	Orig. "Red" A	.473	28.5	734	0.7	0.36	0.18	
	Rejuvenated"Red"E	.631	31	742	0.95	0.36	0.18	
	"Red" from HI	.467	30	741	0.7	0.36	0.18	
	Red from filtrates	.2457	32	73.8	0.4	0.39	0.20	
	"Red" from K salt	.814	27	742	2.7	0.79	0.40	
	" " " "	.674	27	742	2.4	0.85	0.43	
	" " " "	.379	27	742	1.5	0.94	0.47	

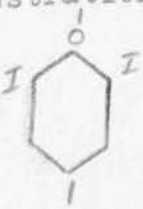
Structure of the "Red" and "White"

A formula for the "Red" and a reaction mechanism for its production may now be proposed. A mechanism for the decomposition of the silver salts of tri-brominated phenols has already been proposed[1] and if we extend it as seems reasonable, to include the catalytic decomposition of the silver salt of the tri-iodo-phenol in ethyl iodide it would be represented by the following equation:

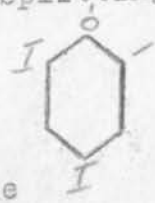




The unsaturated residue left by the abstration of Ag I from the molecule is represented by the formula

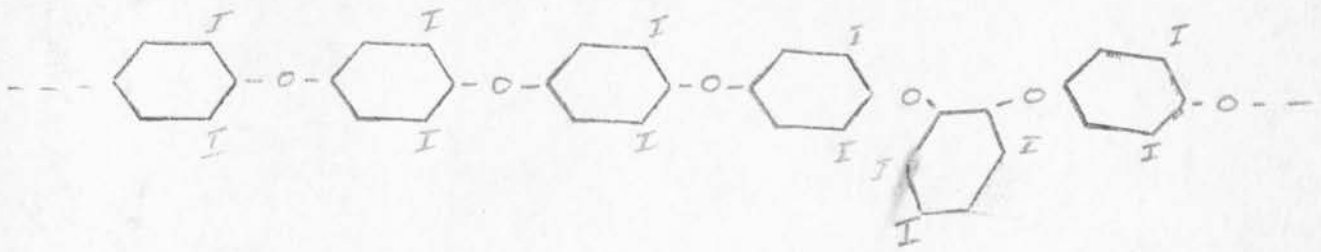


altho the ortho halogen) to some extent.[2] other obvious possiblity (removal of ortho iddine must always be considered to be present This other formula made by splitting out



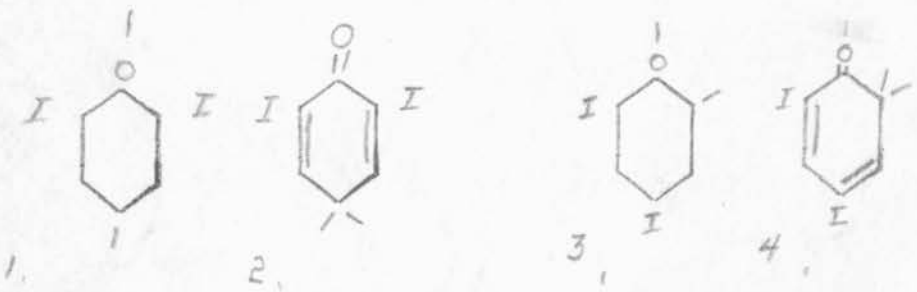
These residues have only a transitory existence, quickly polyverizing to the white poly-di iodo-phenylene oxide which may be represented as a large molecule consisting of an indefinite number of these residues joined thus:

1. J.A.C.S. XXXVIII, 1763, 1916
2. Joyce, -- unpublished work.



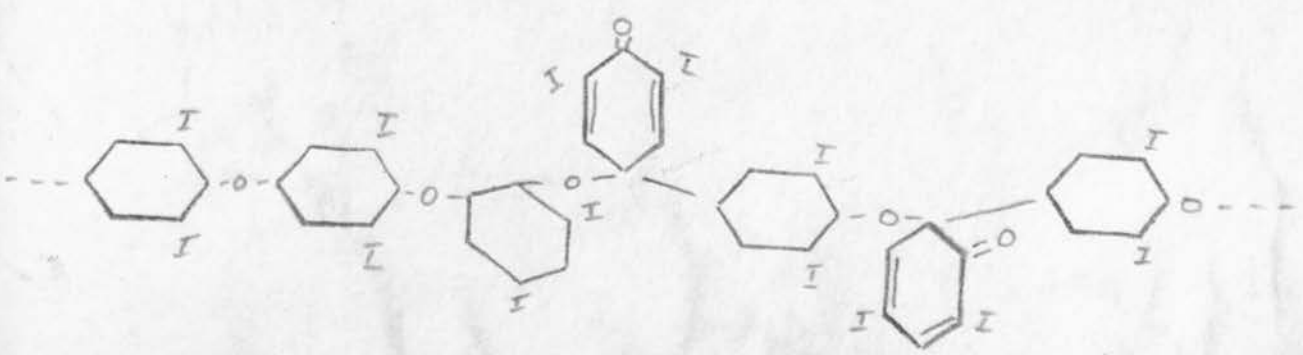
The exact proportion between the ortho and para linkages is not known but it seems now as if the number of para linkages is the larger.

There are four possible forms of these unsaturated residues which must be considered as tautomeric pairs and may be represented thus:



It is apparent that under conditions which produce the white oxides none of forms II or IV take part in the reaction. It is equally apparent that in the formation of the "Red" some of II or IV or both must enter.

At present it is not possible to distinguish between the ortho and para unsaturated residues so that a tentative formula for the "Red" must contain all four and may be represented by the following:



The molecules would probably not be of the same size nor of exactly the same constitution as the proportion of the various groups would vary, as will the actual number of each.

An inquiry into the probable properties of such a mixed molecule show that it would be remarkably like the "Red".

I. Its molecular weight would be high but would vary with the conditions prevailing during preparation.

II. It would certainly be non-crystalline.

III. The individual molecules of any given sample would vary in size, i.e. the determined molecular weights would be averages.

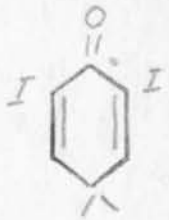
IV. It would not be resolvable into two or more distinct compounds but change in average molecular weight might occur thru loss of smaller molecules.

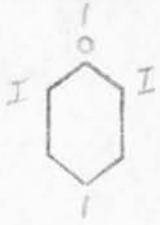
V. It would certainly be colored and would be reducible to a colorless substance. The reduction presents a problem which will be taken up later.

VI. The percentage of quinoid oxygen would vary also according to the number of quinoid residues formed by the conditions prevailing during preparation.

VII. It might polymerize further on oxidation, etd. of the reduction compound.

The Production of the Residue.



The production of a residue of the quinoid type might take place through rearrangements of the other type  or directly from a quinoid form of the salt  Both the silver and the potassium salts of tri-iodo-phenol are colored, suggesting a quinoid form. Either mechanism seems possible and it is not yet possible to distinguish between them, nor is it necessary. The only bit of evidence is the fact that in ethyl iodide the silver salt gives exclusively the white oxide while in water with a catalytic amount of iodine it gives the "Red".

It would seem here that if the form of the salt was responsible for the form of the residue we should get "Red" in both cases. On the other hand a tautomeric residue would be able to assume either form which was favored by the conditions. Hence the tautomerism seems more likely to exist in the residue than in the salt.

It will be seen from the foregoing discussion that Lautemann's Red and the white amorphous bodies have many points in common, most interesting of which is the fact that they are both formed by an apparently identiaal reaction. Cases in which colored substances are formed are assumed to be those in which some of the unsaturated residue has polymerized in the quinoid form.

Reduction.

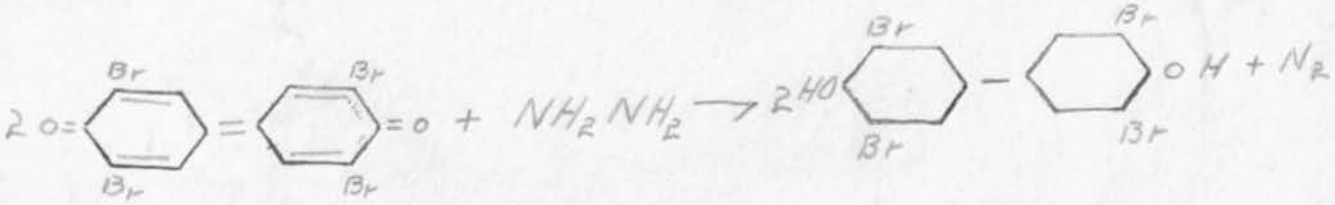
The reduction of a compound of the type 

must take place in one of two ways forming either

or

either of which take 2H per atom of quinoid oxygen. The first is much the more probable as the second would involve splitting a probable c -c tie and also would reduce the molecular weight. No change of molecular weight has been noticed in this direction. Further, it is difficult to see how a compound of the type

could be readily oxidized back to one resembling the original. In either case the per cent of quinoid oxygen would be only half that calculated for the usual reduction of a quinone which for tetra-bromo-diphenylene quinone woule be



The values recalculated according to the abnormal reaction, which we think is more likely the correct one will be found beside those calculated according to the usual reaction in the second of the columns headed o/o quinoid oxygen.

White Oxides by Oxidation.

The oxidation of phenols has given many interesting products, as mentioned in the introduction. Among these may be noted particularly the "Cedriret" type and the "alkali insoluble" substances which are mentioned by Pummerer and Frankfurter[1] as being neither di-nuclear quinones nor oxybiphenyls. The commonest type of oxidation product is of course the simple quinone.

Phenols having the hydrogen on the hydroxyl and the one para to it unsubstituted but with two ortho substituents are stated by Hofmann[2] to give "Cedrirets" on oxidation.

As the phenol mentioned in the literature have not had halogen substituents, we wished to know which of these products our halogenated phenols would give on oxidation.

Oxidation in different solvents such as benzene or carbon bisulphide, with solid oxidizing agents, (PbO_2, MnO_2, Ag_2O) was found to give best results.

Tri-bromo-phenol gave a white amorphous substance apparently identical with the poly-di-bromo-phenylene oxide obtained in other ways. Its bromine content was that called for by $(C_6H_2Br_2O)_n$.

Tri-iodo-phenol gave a similar product, identical with that from the silver salt decomposed in ethyl iodide. No trace of the colored "Red" was present, and it obviously could not have been a reduction product of the "Red".

The case of 2:6 di-bromo-phenol, which should, by Hofmann's rule, give a "cedriret", is interesting as it showed no tendency to go over into dinuclear quinone expected, giving instead only a white amorphous substance apparently like the others.

1. Loc. Cit.

This white substance contained less bromine than is called for by the formula $(C_6H_2Br_2O)_n$ but more than is required by the formula $(C_6H_3BrO)_n$. This shows that some of the ortho bromine has been attacked as well as the para hydrogen.

Para-bromo-phenol and ordinary phenol both gave white amorphous substances apparently like the others. The one from ordinary phenol of which only a small yield was obtained was, as was to be expected, more soluble than the others but still possessed the same preference as to solvents.

These experiments clearly show that oxidation of halogenated phenols, even those having the para hydrogen unsubstituted give rise to the white amorphous oxide type of oxidation product and that this in the case of the s-tri-halogenated phenols is the same as the product obtained from the usual catalytic decomposition of the silver salts.

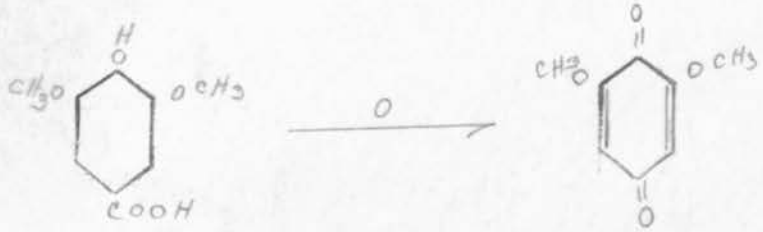
It is interesting to compare these results directly with those obtained by the oxidation of other phenols. In order to save space, only the equations involved will be given, as the references to work not our own are to be found in the introduction.

Mono-nuclear Quinones.

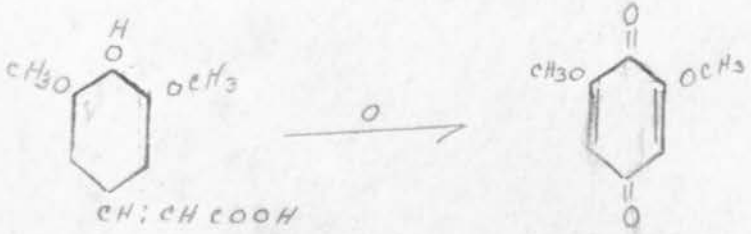
W.Will
B. 21, 602, 2020,1888

Hofmann

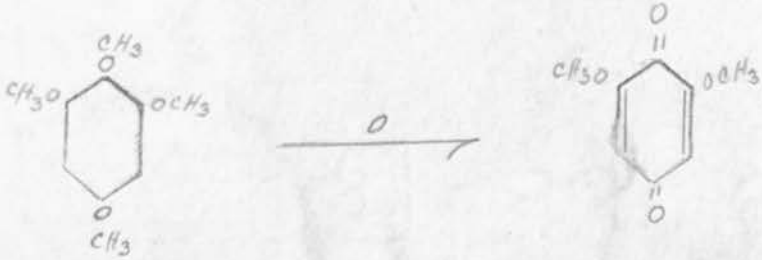
Hofmann



Graebe and Martz

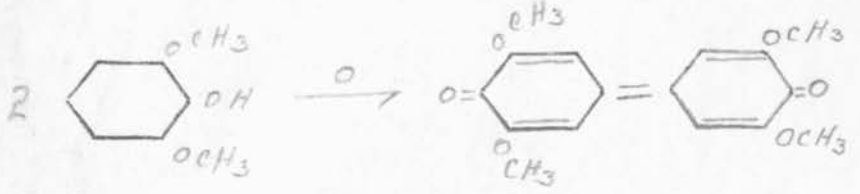


J.Cadamer, B, 13, 30,
2333, 1897.

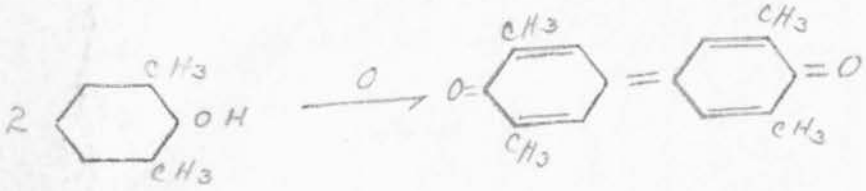


W.Will, 13, 21, 610, 1888

Di- Nuclear Quinones.

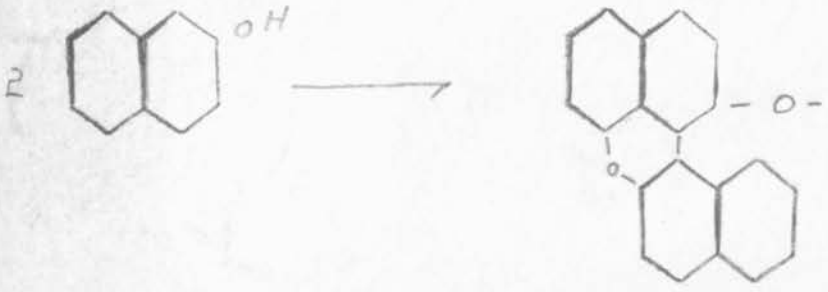


Hofmann

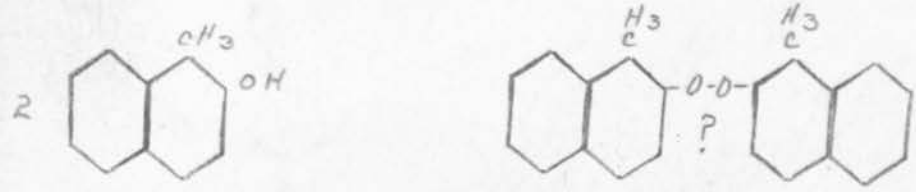


Anwers and Markovitz

Unsaturated Residues.

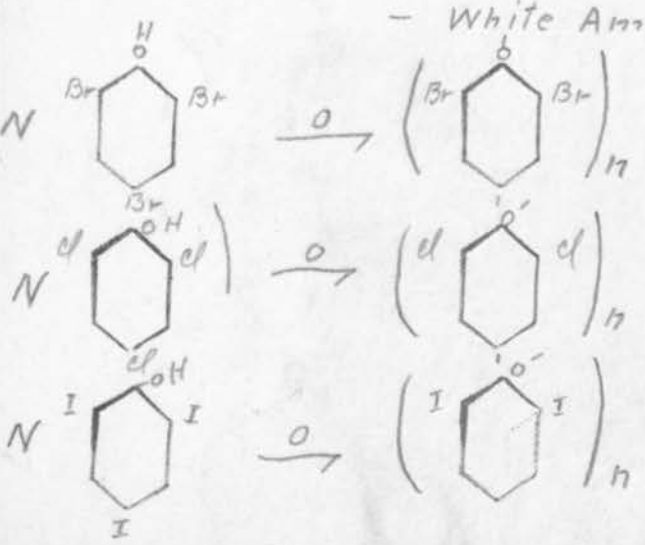


Pummerer and Frankforter



Pummerer and Cherbuliez

– White Amorphous –



White amorphous

White amorphous.

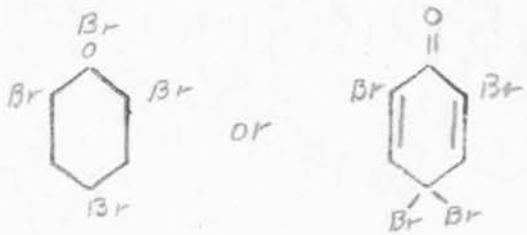
It will be seen that those phenols having methyl or methoxyl in the 2:6 position and with the hydrogen of the hydroxyl or para to it unsubstituted give di-nuclear quinones while those having either of these two hydrogen atoms replaced or having an unsymmetrical arrangement of the methyl or methoxyl groups give mono-nuclear quinones. This is Hofmann's rule.

Where the bromine takes the place of the methoxyl group amorphous products result as seen in the case of 2:6 di-bromo-phenol. Halogen in the para position and also in both ortho positions leads to amorphous products.

The di-nuclear quinones seem to result by oxidation in any medium, the white amorphous products are formed in indifferent solvents. No colored amorphous bodies were obtained in this way.

White Oxides by Reduction.

Removing the hydrogen or substituent from the oxygen of phenols in many cases has led to the formation of white amorphous oxides. A different way of accomplishing this would be by the removal of bromine from tri-bromo-phenol bromide,



This was done by treating the bromide in benzene or chloroform solution with mercury. The result was apparently the same as with the other related reactions, i.e., the "bromide" lost two atoms of bromine leaving poly-di-bromo-phenylene oxide $(C_6H_2Br_2O)_n$.

A similar loss of two atoms of bromine has been described by Kastle[1] who exposed carbon bisulphide solutions of tri-bromo-phenol bromide to sunlight.

Thus, the desired change, the transformation of tri-bromo-phenol bromide by loss of two bromine atoms, has been effected in two ways.

The Mechanism of the Reaction.

We can now consider the most interesting and important question concerned in the various reactions studied, the mechanism of the formation of the various amorphous products. It can be best studied by again comparing the various ways in which they are formed.

They fall naturally under three heads:

I. Decompositions of the phenol salts. $NC_6H_2X_3OM \longrightarrow (C_6H_2X_2O)_n + N(MX)$.

II. Oxidation of the free phenols. $2N(C_6H_2X_3OH)+N(O)\longrightarrow 2(C_6H_2X_2O)_n + N(H_2O) + N(X_2)$

III. Reduction of the phenol bromides. $N(C_6H_2Br_3OBr)+2N(Hg)\longrightarrow (C_6H_2Br_2O)_n+ 2N(HgBr)$

These reactions have some points in common. In each case two atoms are split out, sometimes making a binary molecule. Both ends of the phenol molecule are affected. A high polymer only of the resulting residue is isolated.

The case of the catalytic decompositions of the silver salts when no catalyst other than the solvent is used and also the case of the thermol decomposition of the same salts has been discussed in former papers [1]

It is clear here that at least until the catalytic action of the solvent is better understood we must regard these as strictly intramolecular reactions, as has been suggested.

1. Hunter et al J.A.C.S. XXXVIII,1761, 2474.

In other cases the evidence concerning the order in which the two atoms are eliminated is better.

There are no reactions of any kind on record where it is positively known that the atom para to an active group such as OH or NH_2 is attacked first. In cases in which the substituent is eventually found in the para (or ortho) position, it is assumed by many chemists to have first entered the OH or NH_2 group and to have got to the para position thru subsequent rearrangement. This is the well known theory of "indirect substitution".

In our work, in each case in which white or colored amorphous oxides are formed (with the one exception mentioned, of the silver salts) a substance is used to bring about the reaction which would be expected to abstract only one of the necessary atoms.

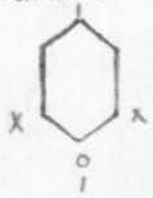
In the oxidations by PbO_2 there can be no doubt that the hydrogen of the hydroxyl is first attacked. In these reactions the active agent could not be expected to react with the atom in the para[1] position and in the case of tri-bromo-phenol bromide it is evident that bromine attached to oxygen would react with mercury far more readily than bromine attached to carbon, indeed it is doubtful if the latter would react at all.

In the silver and alkali salts the catalytic halogen could not be expected to have any particular attraction for halogen in the benzene ring but would have a very strong affinity for the metal attached to the oxygen.

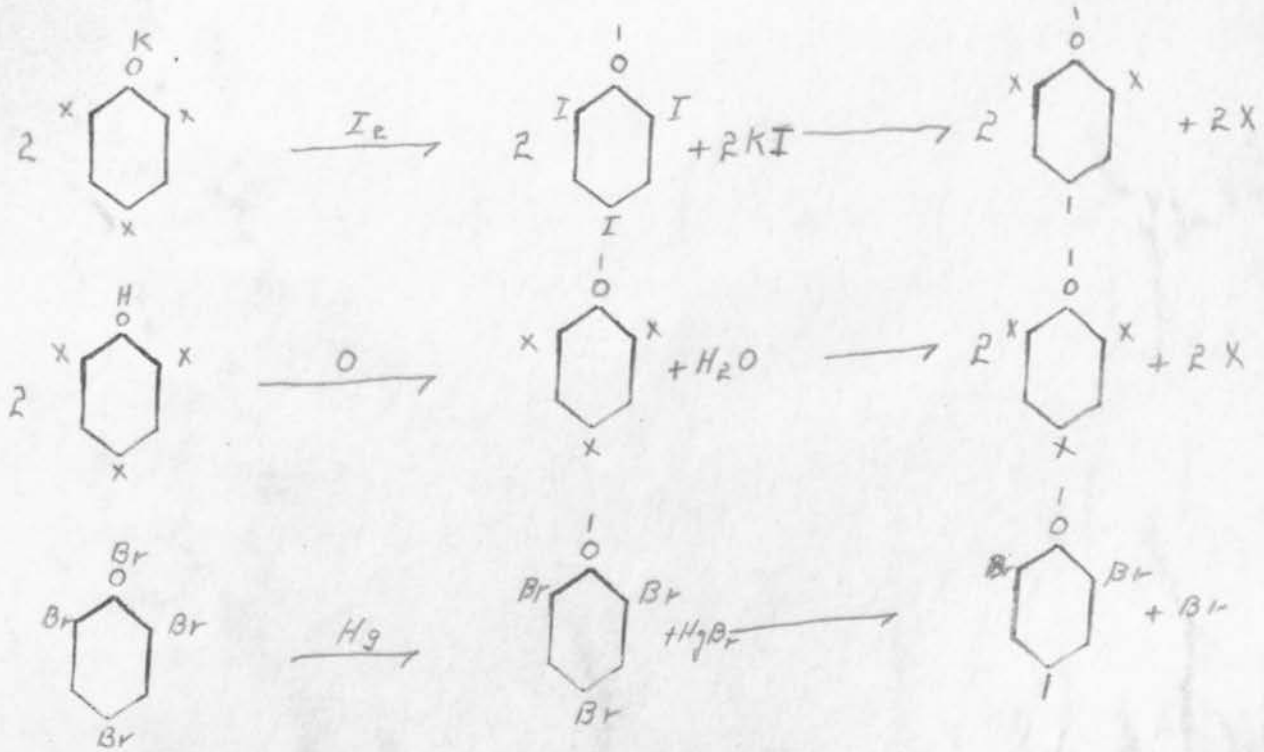
The only other alternative here is to assume the splitting out of the binary compound as such under the catalytic effect of the halogen. This has been proved unlikely by Miss Seyfried[2] who worked with the sodium salt of tri-chloro-phenol in benzene, with iodine as catalyst.

1. What is said here and other places of the para position also applies to the ortho.
2. Unpublished work.

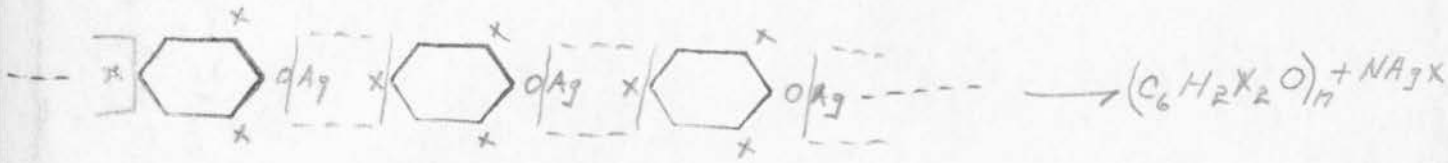
She found much sodium chloride precipitated but found the completeness of the decomposition to depend on the concentration of iddine which would hardly be so if the iodine caused the reaction by its mere presence without entering into it. She also found some chlorine substituted in the nucleus which is a strong argument for the presence of free chlorine at some stage of the reaction.

It is safe to say then that the atom attached to the oxygen is attacked first in all of these, leaving an unsaturated residue expressed by the formula  As the substances isolated are polymers of the residue  it is evident that in a subsequent step of the reaction one more halogen atom is lost, appearing in combination either withe the metal atom of the salt or with the reacting substance.

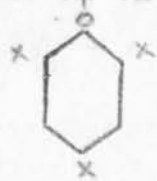
The various types of reaction may then be respresented as follows:

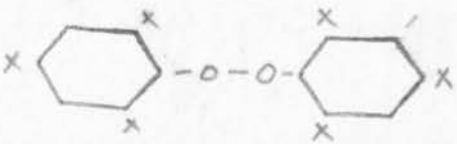


The possibility of an intermolecular reaction for the salts as represented by the following:

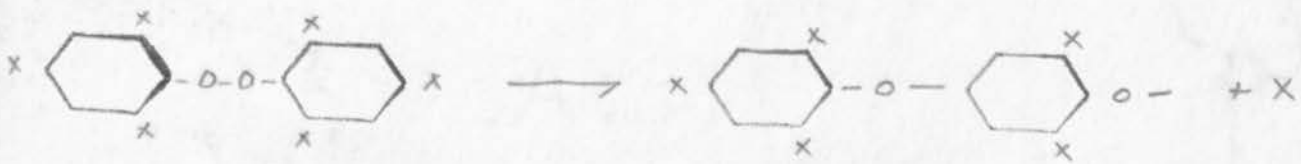


has been discussed in a former paper[1] in which the authors decide against it.

Another possible mechanism may be mentioned here. It assumes the substituent on the hydroxyl to be abstracted as usual leaving the residues  which joins with another one to form a peroxide



which goes through a sort of semidine rearrangement as follows:



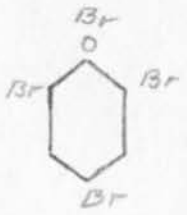
This new radical is then ready to react with a new unsaturated residue and to so dontinue.

This mechanism is not considered seriously here as it is really only a modification of the one adopted and seems unwarranted by the facts at hand now. It should lead to oxides having slightly higher bromine content than that found and at best its only virtue is in giving a means of getting rid of the third halogen atom inside the molecule.

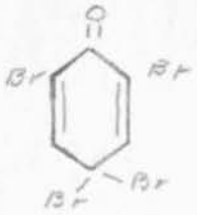
1. J.A.C.S. 38, 1761, 1916.

The various formulae for tri-bromo-phenol bromide may cause some confusion in the work with that substance. The two names and their corresponding formulae are:

Tri-bromo-phenol bromide



Tetra-bromo-cyclohexadieneone



The substance is clearly tautomeric and reacts as if it possessed either formula. We have used the benzenoid formula as best interpreting our results.

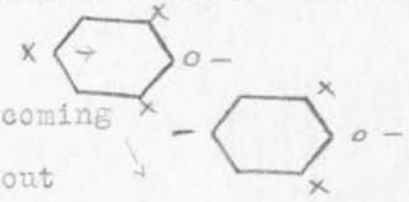
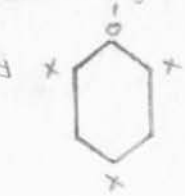
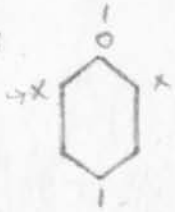
The substance made from this by Benedikt[1] and called by him hexa-bromo-diphenoquinone cannot be ignored. This substance which is made by heating tri-bromo-phenol bromide in a durrent of dry CO_2 to 130°-140°, is a white amorphous substance much like our white oxides in appearance but possessing two marked differences. It is soluble in ether and contains three atoms of bromine per benzene ring as shown by its formula $(C_6H_2Br_3O)_n$.

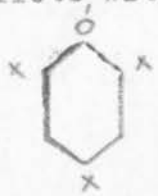
The structure proposed by Benedikt, i.e. hexa-bromo-dipheno quinone is clearly wrong as it has been found by Olivier[2] to have a molecular weight of the same order of magnitude as the poly-di-bromo-phenylene oxide. It has neither color nor oxygen reducible by hydrazine.

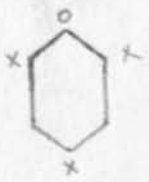
No acceptable structure for it has been put forward and we do not intend to speculate upon one now as the disposition of the third bromine atom presents a problem which has not yet been solved. We are only interested in it at present insofar as it bears upon

1. Loc. Cit.
2. Loc. Cit.

the problem in hand.

Our theory of the production of the white and the colored oxides rests upon the assumption that the residue  is unstable and loses one atom of halogen, becoming which then polymerizes. This has been borne out by experiment as in every case in which a radical would be expected for the formula  we get instead a polymer of a hypothetical radical containing one less atom of halogen,  .

At first glance the formation of a similar substance to the di-bromo oxides, but containing one more atom of bromine conflicts with this view, assuming polymerization of the radical: 

A residue of this form could not polymerize to the extent found in Benedikt's substance $(C_6H_2Br_3O)_n$ without at least a rearrangement. This then instead of being contrary to our view is another point in proof that residues of the type  are unstable, for with only one free valence its power to polymerize is limited to simple doubling.

It must be remembered that this reaction takes place at relatively high temperatures, and that if sunlight is used instead of high temperature we get the usual residue having two atoms of halogen, by the loss of two others.

An interesting point may be made here in regard to the analog of the above compound, tri-chloro-phenol bromide.

When this is heated to 130°-140° in a stream of dry CO_2, it gives off both chlorine and bromine, the proportion being about 5 molecules of bromine to one of chlorine. This is strong evidence that some of the compound is in the quinoid form but if all of it were in that form one would expect a larger proportion of chlorine to be given off than was found.

A method of making Benedikt's substance has also been given by Kastle and Loevenhart.[1] They claim to have prepared it by the action of chloroform solutions of tri-bromo-phenol bromide upon the silver salt of tri-bromo-phenol. Knowing the instability of this silver salt in the presence of free halogen we considered this synthesis very doubtful and upon repeating the work got the results we expected.

The reaction was carried out according to Kastle and Loevenhart's directions. The amount of amorphous oxide obtained accounted for practically all of the silver salt assuming the usual catalytic decomposition to have taken place. The oxide on analysis proved as we had forseen, to be our poly-di-bromo-phenylene oxide and not Benedikt's substance.

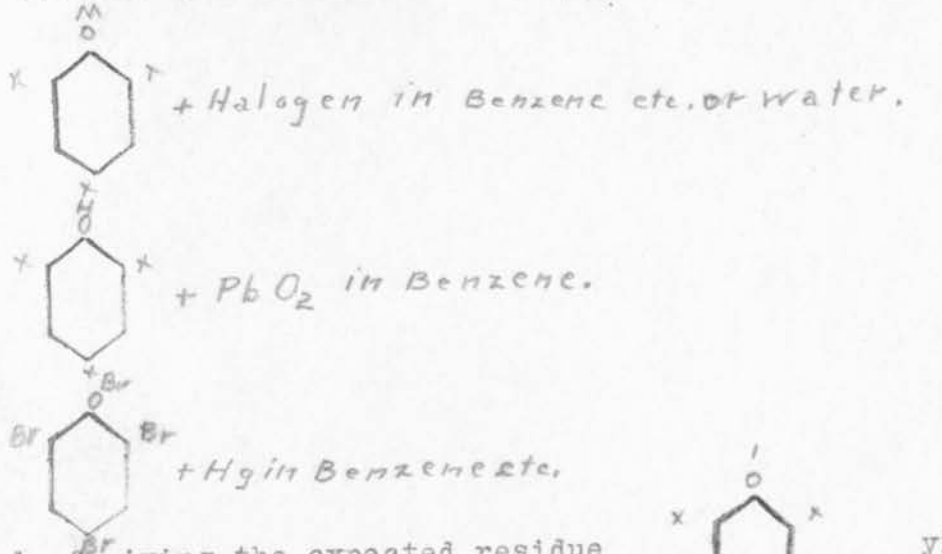
In other experiments the amount of unchanged tri-bromo-phenol was estimated and 60 o/o accounted for. The other 40 o/o was not accounted for but a considerable production of orange tarry material may account for this loss, as orange tarry material is a continued nuisance when working with tri-bromo-phenol bromide. Tri-bromo-phenol was identified in the alcoholic liquor from which the amorphous body was precipitated.

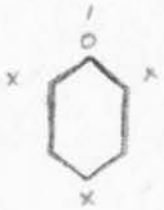
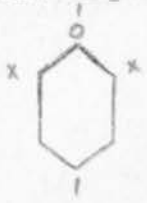
1. J.A.C.S. 27, 31, 1902

It is clear that here as far as the silver salt is concerned we are dealing with the usual catalytic decomposition. In this case the bromide furnishes the free bromine or itself acts as the catalyst. At any rate no appreciable amount of Benedikt's substance is formed, contrary to the belief of Kastle and Loevenhart. These various facts lead us to believe that Benedikt's compound need not be considered as in any way contradictory to our theory of the reactions.

Summary.

It has been shown that the three systems



instead of giving the expected residue  yield polymers of the residue 

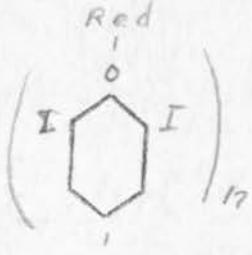
The first residue is assumed to lose halogen forming the second.

The products of these reactions are colorless or colored amorphous bodies of identical composition and similar properties.

The reactions yielding the colored products are

in the presence of water; the others yield white compounds.

The colored substances have been shown not to be di-nuclear quinones.

The case of 

has been investigated, it has high molecular wieght (2300)4800), about 12 o/o of its o oxygen is quinoid, it is not a mixture of two or more distinct types of compounds, it can be reduced, reoxidized and acetylated with very little change in composition.

The residue of which these substances are composed is assumed to exist in four tautomeric forms:

We conclude that:

The white substances are polymeric containing various proportions of I and III. The colored substances contain various proportions of all four forms. The number and variety of reactions leading to these amorphous bodies shows that their production from the silver salts in ethyl iodide which was so unexpected, is only one of a large number of reactions yielding similar products. These indicate a strong tendency of derivatives of symetrically trihalogenated phenols to give these unsaturated residues.

EXPERIMENTAL PART.

The Potassium Salt of Triiodophenol.

Preparation.

Attempts were first made to prepare the salt from water solution. A small quantity of KOH solution was saturated with tri-iodo-phenol slightly below 100°. The solution cooled and the crystals filtered off and washed with a very small quantity of water.

The extreme solubility of the salt in water made this method unsuccessful. Further, it was found almost impossible to dry the salt made in this way on account of its great sensitiveness to heat etc., while damp and not in presence of excess alkali. Alcohol and acetone were tried as solvents without giving much promise of success.

The method which gave best results and which was finally used to prepare the pure samples used in the following experiments was a modification of the method of Atkins and Wilson (1) for preparing anhydrous sugars.

Fifteen grams of pure tri-iodo-phenol of melting point 156°-156½° were dissolved in 125 c.c. benzene. Two grams KOH were dissolved in 1 c.c. water and 50 c.c. absolute alcohol. The two solutions were mixed in a distilling flask and the solvents were distilled off, the temperature being noted. The distillation was stopped when the salt precipitated. It was usually necessary to add 100 c.c. more benzene before this point could be reached

(1) Soc. 107, 1915, 916.

without going too near dryness. The temperature at the end was above 79°.

The gray-yellow precipitate of crude salt was filtered off from the small quantity of solution washed with benzene and recrystallized from the minimum quantity of absolute alcohol, in which it is very soluble.

Crystallization was carried out in partial vacuum both for the evaporation and cooling effects.

The crystals were gray with a yellow tinge; they turned yellow on slight warming either alone or in benzene and decomposed at about 75° in air.

A sample of this salt, after standing several weeks in a dessicator over $CaCl_2$ and ceresine, to remove trace of benzene, analyzed for iodine by Carius' method.

Weight substance	.1402 g.	.1037 g.
Weight Ag. I	.1833 g.	.1347 g.
% I found	70.64	70.18
Calculated for	$C_6H_2I_3OK$,	74.66%
Calculated for	$C_6H_2I_3OK \cdot C_2H_5OH$	68.50%

Another sample from alcohol dried in vacuo over $CaCl_2$ and ceresine without heat was analyzed for iodine and potassium.

For Iodine.

Weight substance	.2803 g.	.2807 g
Weight Ag. I	.3542 g.	.3532 g
% I found	68.30	68.02
Calculated for	$C_6H_2I_3OK \cdot C_2H_5OH$	68.50%

For Potassium

Weight Substance	.2686 g.
Weight K_2SO_4	.0429 g.
% K found	7.17
Calculated for	$C_6H_2I_3OK \cdot C_2H_5OH$ 7.05%

This sample was gray-yellow in color.

Purification of the Salt.

Two grams of this salt were dissolved in 1 c.c. absolute alcohol and 20 c.c. benzene added. This solution was evaporated in vacuo till a considerable precipitation had occurred, a suitable amount of mother liquor being left. The precipitate was then filtered off and washed with benzene. The crystals obtained were nearly colorless while cold and fresh; they turned yellow however, on standing or more rapidly on gently warming.

A sample of this salt was dried at 50°-70° for half an hour and analyzed for iodine. The sample was lemon yellow.

Weight Substance	.1479 g.
Weight Ag. I	.2075 g.
% I found	74.89
Calculated for $C_6H_2I_3OK$	74.66

Some of this salt, after two recrystallizations from benzene-alcohol, was dried at 80° and analyzed for iodine.

Substance	.1103 g.	.1555 g
Weight Ag. I	.1511 g.	.2145 g.
% I found	74.01	74.53
Calculated for	$C_6H_2I_3OK$	74.66

More of this sample was dried by heating slowly to 90° and analyzed for potassium.

Substance	.2924 g.	
Weight K_2SO_4	.0502 g.	
% K found	7.71	
Calculated for	$C_6H_2I_3OK$	7.65

All dried samples were yellow and no deepening in color was noticed on standing a year.

Experiments on the Potassium Salt.

Solubility.

The salt was found to be extremely soluble in water, alcohol and acetone; less soluble in ether and pyridine and insoluble in benzene and chloroform.

The salt dissolved in a small quantity of water to a clear solution; the addition of more water caused the separation of white flocks which a trace of alkali redissolved.

The pyridine solution was remarkable because of its deep yellow color.

The salt could not be recovered from etherial solution as it invariably decomposed on evaporating off the ether.

Effect of Bromine Vapor Etc.

One of the first effects noticed in working with the potassium salt was that solutions containing it threw down a deep purple precipitate on coming in contact with small quantities of bromine vapor.

A few grams of the salt which had been crystallized from alcohol were wet with water and exposed to a small quantity of bromine vapor for a few seconds. It turned purple immediately and after warming to about 40°, the change seemed to be complete.

The purple product was washed thoroly with water and with alcohol, then dried at 100° and in the dessicator

to constant weight, and analyzed for iodine.

Weight Substance	.1658 g.	.1200 g.
Weight Ag. I.	.2246 g.	.1635 g.
% I. found	73.20	73.62

Calculated for "Lautemann's Red" $(C_6H_2I_2O)_n$ 73.82

Other samples of potassium salt were exposed to the action of small quantities of bromine and iodine both with and without warming. The results in all cases were apparently the same, the change taking place more rapidly on gentle heating.

Some of the dry salt, crystallized from benzene-alcohol mixture, was exposed to a small quantity of bromine vapor; it immediately darkened on the surface. The change did not seem to proceed much beyond this nor did the darkened part show the characteristic purple color. On wetting the sample, however, the purple color appeared and the change proceeded thru the remainder of the salt.

Extent of the Change.

A small amount of the salt crystallized from alcohol, was dissolved in 5 c.c. CO_2 free distilled water in small flask and to this was added two drops of $\frac{N}{50}$ Br_2 solution. Purple spots appeared immediately where the drops fell. The flask was corked up and left over night, after which time considerable purple compound was found. This was filtered off, dried at 100° and weighed.

Weight Salt .2191 g.

"Red" obtained .1307 g.

% "Red" found 59.65

Calculated $(C_6H_2I_2O)_n$ from $N(C_6H_2I_3OK \cdot C_2H_5OH)$ 62.96

This purple compound corresponds in every respect to the "Lautemann's Red" to be described later.

Effect of Light.

Two samples of potassium salt of about .1 gram each were placed in two small vials with 1 c.c. CO_2 free water and tightly stoppered.

Number I was placed in a window not in direct sunlight and began to show purple in two days, the amount slowly increasing for several days, apparently complete on the fifth day.

Number II was kept in subdued light and showed no change in six days. On the seventh day it was placed in direct sunlight and showed purple traces in fifty minutes. The change was apparently complete in twenty-four hours and evidently proceeded after removal from sunlight.

In both cases, the first traces of color appeared in the thin part of the meniscus between solution and glass.

A sample weighing .1694 grams was dissolved in five cubic centimeters CO_2 free water in a small flask, corked and kept in diffused light for two days; no purple developed.

It was placed in sunlight on the third day and after completion of the change, (several hours), the precipitate was filtered off on a Gooch filter, washed with water and alcohol, dried at 100° and weighed.

Weight substance	.1694 g.	
Weight of "Red"	.1043 g. or	61.57%
Calculated for		62.96%

Effect of Heat.

A quantity (3-4 grams) of the salt crystallized from alcohol was heated on the water bath. It turned dark slowly and then gave off a puff of iodine vapor. The residue appeared to be a mixture of purple and gray grains.

Another sample just filtered from alcohol was put in an oven to dry, the temperature being 90°-100°. This sample turned purple quietly and slowly and was removed before all had changed.

Samples placed in a melting point apparatus, showed the change would take place at about 75°.

It was found possible to heat the "dry" salt, (that crystallized from benzene-alcohol), to 90° with safety and to 100° for a short time. Above this, the salt turned gray and darkened in places and if left for a time apparently all turned black instead of purple, the black product being insoluble in CS_2.

In the melting point apparatus, the "dry" salt remained yellow to 100°; above this became discolored,

gray first and finally brown at 160°-165°, no further change noticed up to 210°, except a gradual evolution of iodine, which began slightly above 100°; no sudden changes occurred.

Effect of Low Temperatures.

Two varieties of this salt have been described, a gray (yellow) hydrated (alcoholic) form and a yellow anhydrous form. On heating, both of these forms show an increase in yellowness before decomposition temperatures are reached.

On cooling in an ice-salt mixture, both show a slight diminution in color, though the change is not marked. When samples of both sorts were placed in thin glass tubes and immersed in a mixture of solid CO_2 in ether, both became nearly colorless. The color was quickly regained on warming them slightly above room temperature.

A marked diminution in color of the silver salts of tri-iodo-phenol, tri-bromo-phenol and tri-chloro-phenol was noticed under the same treatment.

The red silver salt of tri-bromo-phenol became almost yellow.

The Potassium Salt of Tri-bromo-phenol.

Attempts were made to prepare this salt in the same way as the salt of tri-iodo-phenol. The method was found unreliable as on several occassions, the salt decomposed while driving off the solvents.

One such case was investigated. Just before the boiling was to be discontinued, a sudden frothing of the mixture was noticed, accompanied by a subsequent re-solution of most of the precipitated salt.

The remaining precipitate was found to be KBr. The liquid consisted mostly of a solution of white amorphous compound in benzene. This was isolated in the usual way, i.e. precipitation with alcohol and repeated re-solution and re-precipitation by $CH\ Cl_3$ and alcohol. It was dried and analyzed for Br.

Substance,	.1535 g.	.1471 g.
Weight of Ag Br	.2333 g.	.2217 g.
% Br found,	64.68	64.14
Calculated for $(C_6H_2Br_2O)_n$		64.00

It had every appearance of and the same solubilities as Hunter's poly-di-bromo-phenylene oxide.

The salt was finally made by using the same method except that evaporation was carried on in vacuo, the temperature being kept between 29° and 35°.

Two grams of KOH dissolved in 1 c.c. water and 50 c.c. absolute alcohol, 15 grams tri-bromo-phenol in 100 c.c. benzene. The solvents were boiled off in vacuo (3-4 cm. Hg.).

The salt precipitated was filtered off, washed with benzene and recrystallized from a little alcohol and much benzene.

This salt did not dissolve entirely in water but after boiling for about half an hour with $CHCl_3$ in which it is insoluble, but which dissolves tri-bromo-phenol, it appeared to be pure.

Only a white variety was found. It had the same solubilities as the tri-iodo salt. The pyridine solution was yellow; yellow crystals were obtained from this solution but were not analyzed.

Effect of Heat, Bromine etc.

Heating this salt without water gives a white amorphous compound and KBr. Heating with water, if previously exposed to bromine vapor, gives an orange colored amorphous compound and KBr.

A sample of this salt was wet with water and exposed to bromine vapor and heated on the water bath for a few minutes. The amorphous compound was extracted with benzene and precipitated by alcohol.

Some white compound always accompanies the orange and was partially separated by repeated fractional precipitation from benzene by alcohol. The orange substance being the more soluble.

The most deeply colored fraction was dried and analyzed for Br.

Substance,	.1522 g.	
Weight Ag Br	.2300 g.	
% Br found	63.53	
Calculated for	$(C_6H_2Br_2O)_n$	64.00

Lautemann's Red. (1)

Methods of preparing this substance from the Silver salt and the potassium salt of tri-iodo-phenol have already been described.

A more convenient method for making it in quantity has been described by Kammerer and Benzinger[2], whose method, slightly modified, was used in preparing the samples used in the following work where not otherwise designated.

The method as used by us consisted in treating a solution of 10 grams of phenol and 111 grams Na_2CO_3 dissolved in 1000 c.c. water at the boiling point, with a KI_3 solution containing about 100 grams I_2 and 75 grams KI. The KI solution was added till free iodine remained present in the mixture. It was then treated with dilute sodium thiosulphate solution to remove the excess iodine, filtered off and thoroughly washed with water and alcohol.

The resulting substance, "Lautemann's Red" is a deep purple powder, insoluble in all aqueous solvents, alcohol and ligroin; quite soluble in CS_2 and $C_2H_4Br_2$ and $CHBr_3$ from which it is precipitated by alcohol or ligroin. It is remarkably inert and resistent to vigorous reagents.

The crude "Red" so obtained was purified in various ways.

First by simple washing with alcohol and subsequent drying at 100°; this is designated crude "Red".

(1). Lautemann A, 120, 309, 1861

(2). Ber. XI, 557, 1878

Second, by digestion in alcohol for 1-2 hours at boiling point, designated "Red" purified by alcohol.

Third, by solution in C S_2 and precipitation by ligroin, designated "Red" from CS_2.

Fourth, from solution in bromoform or ethylene dibromide by ligroin or alcohol and designated "Red" from the solvent used. This last was found to be, by far, the best method of purification and was used to the greatest extent.

When either method three or four was used, a small part of the crude "Red" was always found to be insoluble; this was saved, dried and designated, insoluble "Red".

Experiments on "Lautemann's Red".

Reductions.

A sample of "Red" purified by alcohol, was mixed with tin and strong hydrochloric acid and heated, now and then, for several days. It gradually turned white; it was filtered off, washed and dried and dissolved in $C S_2$ to faintly straw colored solution (when concentrated). Ligroin precipitated it from this solution as white flocks, apparently identical with the original "Red", except in color.

The $C S_2$ solution of this reduction product, when shaken with $Pb O_2$ or $Mn O_2$ developed a deep purple color and ligroin precipitated the substance as deep purple flocks, apparently identical with the original "Red".

No iodine or other crystalline substances (other than chlorides of tin) could be found in the tin-hydrochloric acid filtrate.

The effect of zinc and dilute sulphuric acid was apparently the same, except the bleaching was more rapid.

Reduction by H I.

Ten grams of "Red" from $C S_2$, 200 c.c. concentrated H I and ten grams of red phosphorus were mixed in a flask fitted with a reflux condenser by a ground joint and the mixture boiled gently for 29 hours. The red rapidly lost its color, leaving the somewhat different shade of the red phosphorus.

The insoluble part was filtered off, washed and dried. The reduction product was extracted with $C S_2$ and precipitated by ligroin. It came down as snowy white flocks and after drying, weighed seven grams.

Nothing crystalline could be found in the H I solution. The red phosphorous residue was treated with water and iodine till all of the phosphorous was gone; a small insoluble colorless and non crystalline residue was found.

One half of this product was shaken with 20 c.c. $C S_2$ and 10 grams $Pb O_2$ for about half an hour. The filtrate from this was precipitated with ligroin and the resulting "Red" filtered off and dried.

This was analyzed for iodine.

Substance	.1143 g.	
Ag I	.1521 g.	
% I found		71.90
Calculated for $(C_6H_2I_2O)_n$		73.82

A sample was purified by solution in bromoform and precipitation by ligroin.

Substance	.1100 g.	
Ag I	.1467 g.	
% I found		72.06
Calculated for $(C_6H_2I_2O)_n$		73.82

A sample of the reduction product was purified by bromoform and analyzed.

Substance	.1283 g.	
Ag I	.1719 g.	
% I found		72.39
Calculated for $(C_6H_2I_2O)_n$		73.82

Molecular weights and other determinations were made on these two substances which appear below and also in the table (page 18) under the head of "Red" reduced by H I, and regenerated "Red" from H I.

Molecular Weights.

These were taken cryoscopically in Ethylene dibromide purified by freezing twice.

The "Red" Reduced by H I.

Substance	.5122 g.	.7242 g.
Weight Solvent	50. g.	50. g.
Δ	.035	.036
Molecular Weight	3435	4747

Re-oxidized Reduction Product

Weight Substance	.5587 g.
Weight Solvent	50. g.
Δ	.032
Molecular Weight	4123

Reduction by Hydrazine

Three grams of Crude "Red" were wet with alcohol and treated with .5 gram hydrazine sulphate and 25 c.c. N/5 K O H. This mixture was heated on the water bath. It bleached rapidly to a faint pink, after which no further change occurred in fifteen minutes. The reduction product was isolated and dried; it was faintly pink. On solution in C S a small amount, (10%), of insoluble "Red" was found: the product precipitated from this solution was entirely

white.

A sample of "Red" from C S_2 was reduced in the same way by hydrazine and was entirely bleached in fifteen minutes.

The reduction product from each of these experiments was re-oxidized to a "Red" by Pb O in C S_2.

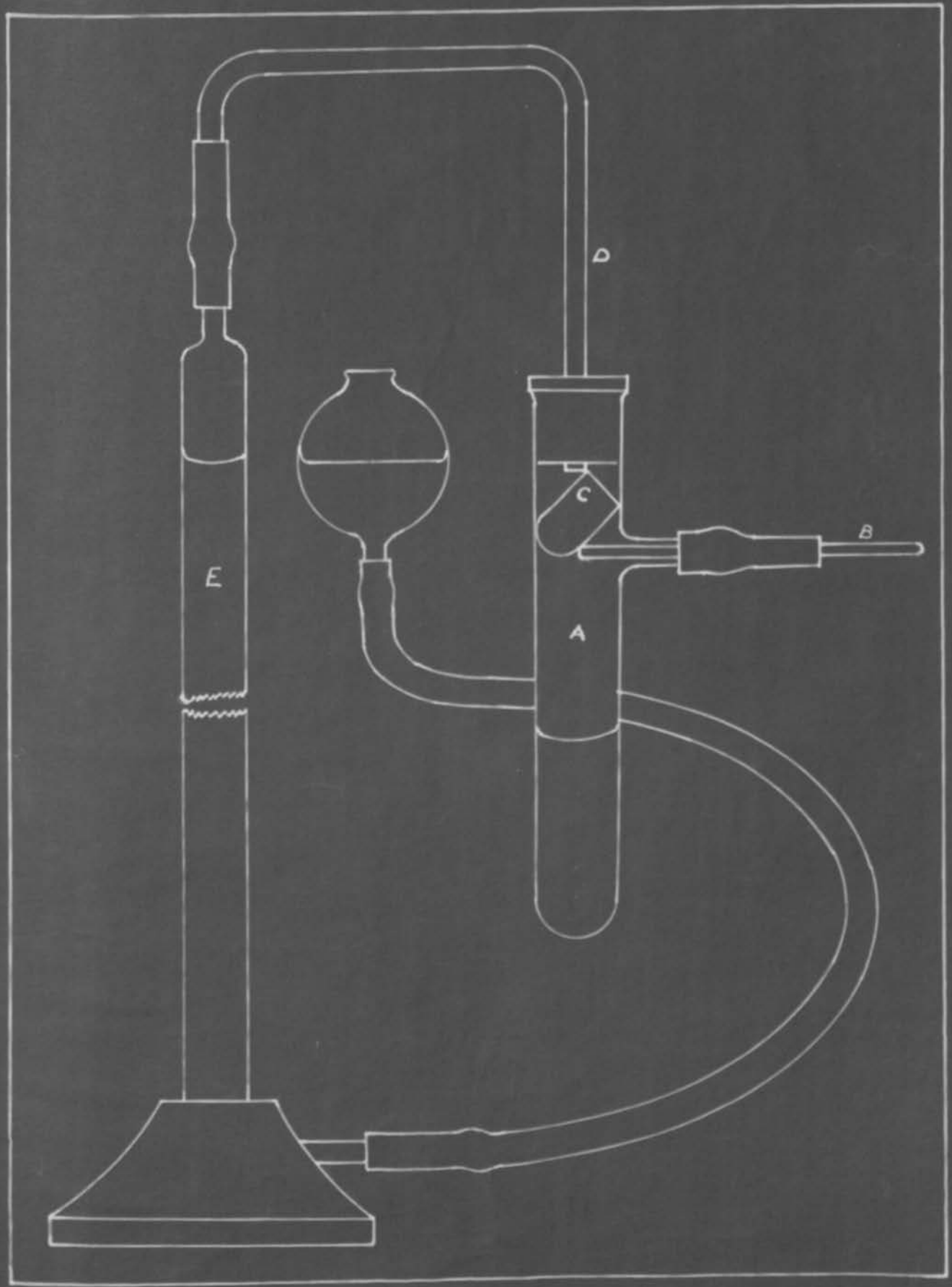
Determination of Quinoid Oxygen.

Use was made of the reducing action of hydrazine on the "Red", the evolved nitrogen being taken as a measure of the quinoid oxygen present. The determination was carried out in the apparatus diagrammed on page 61 .

In using the apparatus, about one gram of the sample was placed in the small tube C which was then placed in position above the trigger B in the side arm test tube A, containing one gram saturated K O H solution, nine c.c. water and one half a gram hydrazine sulphate.

The test tube was connected to the gas burette by the glass and the rubber connection indicated the level of the water read off at atmospheric pressure, after the whole had stood for about half an hour to reach room temperature which was noted.

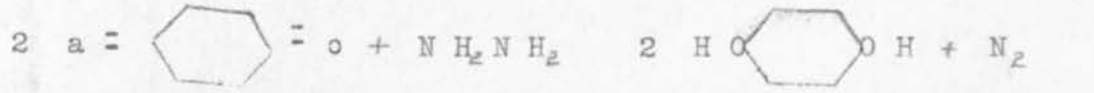
The trigger B was then pulled, allowing the sample to fall into the hydrazine solution and after shaking, to insure thoro mixing, the whole was allowed to stand till no further change took place, usually about twenty to thirty minutes. The temperature and pressure were again taken and the volume of gas read off. The difference in gas volume readings is designated N_2 in the table. Quicker results were obtained if the very dry


D
C
B
E
A

amorphous materials were first wet with alcohol. This did not seem to affect the process in any other way.

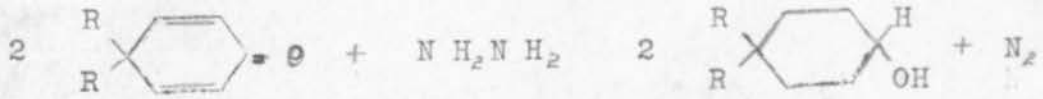
Values for some known quinones are given below.

It was assumed that the following reaction took place:



which holds for mono- and di-nuclear quinones which do not form hydrazones under these conditions.

If the following reaction takes place, which is not improbable in some cases, the per cent of quinoid oxygen must be halved.



Tetra-bromo-dipheno-quinone.

Weight substance	.5034 g.	.4700 g.
Temperature	32°	32°
Pressure	73.8 cm.	73.8 cm.
Evolved N_2	13.8 c.c.	12.55 c.c.
% Quinoid O. found	6.57	6.42
Calc. % Quinoid O	6.40	

Cedriret

(Tetramethoxy-dipheno-quinone)

Weight substance	.1752 g.
Temperature	32°
Pressure	74.6 cm.
Evolved N_2	7.6 c.c.
% Quinoid O found	10.57
% Quinoid O calc.	10.53

"Red" Purified by Alcohol.

Weight substance	.593 g.	.925 g.	.663 g.
Temperature	30°	28°	28°
Pressure	74.0 cm.	74.2 cm.	74.0 cm.
Evolved N_2	0.9 c.c.	1.6 c.c.	2.1 c.c.
% Quinoid O found	0.36	0.40	0.75
Calc. for $(C_6H_2I_2O)_2$	4.65		

"Red" from $C S_2$

Sample I

Weight substance	1.324 g.	.7365 g.
Temperature	33°	30.5°
Pressure	74.1 cm.	74.0 cm.
Evolved N_2	4.1 c.c.	2.5 c.c.
% Quinoid O found	0.75	0.81

Sample II.

Weight substance	.9790	.9130
Temperature	33°	31°
Pressure	74.0 cm.	74.0cm.
Evolved N_2	3.9 c.c.	3.5 c.c.
% Quinoid O found	0.95	0.91

Samples III, IV & V.

Weight substance	.579 g.	.613 g.	.768 g.
Temperature	28°	28.5°	30°
Pressure	74.2 cm.	73.4 cm.	74.0 cm
Evolved N_2	1.0 c.c.	1.0 c.c.	1.5 c.c
% Quinoid O found	0.41	0.39	0.47

Acetylations.

Two grams of crude "Red" were heated on the water bath under a reflux condenser with 15 c.c. acetic anhydride and a few mg. $FeCl_3$ for ten hours. It turned white; no further change was noticed.

The experiment was repeated, using 4.5 grams of purified "Red", 20 c.c. anhydride and boiling 14 hours. It was not completely bleached, and on boiling with a second charge of acetic anhydride, it blackened somewhat. Several other samples showed the same tendency. The "White" from these acetylations could not be changed to "Red" by PbO_2 in CS_2.

Hydrolysis of Acetyl Derivative.

Five grams of the acetylation product from a 20 gram sample were boiled with 1 gram KOH, 60 c.c. water and 40 c.c. alcohol for three hours. No apparent change took place but this product on shaking with CS_2 and PbO_2 gave a "Red" apparently like the original.

It was later found that acetylation proceeded more rapidly and without blackening, if the "Red" was first reduced with hydrazine. The product seemed to be the same in either case.

The product from direct acetylation was analyzed for I.

Substance	.1173 g.	.1048 g.
Ag I	.1564 g.	.1403 g.
% I	72.04	72.33

Calculated for $C_6H_2I_2O \cdot 1/6\ CH_3CO$ 72.36

Further Manipulation of the "Red".

A twenty-seven gram sample of "Red" from C S_2 was carried through all of these processes in the following way, each step being analyzed etc.

Two and one half grams were saved, purified by $C_2H_4Br_2$, and called Original "Red" A.

Analysis for Iodine.

Weight substance	.1407 g.	.1085 g.
Weight Ag I	.1915 g.	.1471 g.
% I found	73.54	73.25
Calculated for $(C_6H_2I_2O)_n$		73.82

Molecular Weight.

Solvent, Ethylene dibromide.

Weight substance .5342 g.

Weight solvent. 50 g.

Δ .026°

Molecular Weight 4847

Molecular weights of some other samples of "Red" are given below:

"Red"from Potassium Salt

Weight substance 1.0741 g.

Weight solvent ($CHBr_3$) 100. g.

Δ .055°

Molecular weight 2810

"Red" Purified by Alcohol.

Several Different Samples.

Weight substance	.2428 g.	.8131 g.	.6386 g.
Weight solvent ($C_2H_2Br_4$)	100. g.	100. g.	100. g.
Δ	.015°	.050°	.029°
Molecular Weight	2331.	2300.	3136.

Determination of Quinoid Oxygen.

Original "Red" A.

Weight of substance	.473 g.
Temperature	28.5
Pressure	73.4 cm.
Evolved N_2	0.7 c.c.
% Quinoid O found	0.36

Reduction.

The rest of the twenty-seven gram sample was mixed with thirteen c.c. concentrated K O H solution, one hundred fifty c.c. water and five grams hydrazine sulphate and heated on the water bath. The reaction began in the cold, proceeded rapidly with effervescence on heating and was apparently complete in fifteen to twenty minutes. The "Red" bleached out entirely; no other change could be detected. The reduction product was filtered off and washed with water and alcohol and dried; twenty-two grams were obtained, of which five grams were saved, purified by C H Br_3 and alcohol and called reduced "Red" B.

Analysis for Iodine.

Weight substance	.1364 g.
Weight Ag I.	.1849 g.
% I found	73.24
Calculated for $(C_6H_2I_2O)_n$?	73.82

Molecular Weights

Solvent, ethylene dibromide.

Weight substance	.5578 g.	1.0653 g.
Weight solvent.	50 g.	50. g.
Δ	.029°	.051°
Molecular Weight	4539.	4951

No quinoid oxygen.

Acetylation.

Seventeen grams of the reduction were heated with 75 c.c. acetic anhydride and 0.1 gram $FeCl_3$ over the free flame for four hours, after which time, a sample tested, failed to give a "Red" with PbO_2 and CS_2. Four grams were saved, dissolved in CS_2 and precipitated with ligroin, also precipitated from bromoform, and designated acetylated "Red" C.

Analysis for Iodine.

Weight substance	.1169 g.	.1147 g.
Weight Ag I	.1562 g.	.1526 g.
% I found	72.19	71.88
Calculated for		
$C_6H_2I_2O \cdot 1/6\ COCH_3$		72.36

Molecular Weights

Solvent, ethylene dibromide.

Weight substance	.5075 g.	1.0172 g.
Weight solvent	50. g.	50. g.
Δ	.026°	.058°
Molecular Weight	4607	4765.

No quinoid Oxygen.

Hydrolysis.

Eleven grams of the dried acetylation product were heated on the water bath with 100 c.c. alcoholic KOH, containing 5 c.c. concentrated aqueous KOH, for two hours. The product was filtered off and boiled with 75 c.c. water and 10 c.c. strong KOH solution for half an hour, after which it was filtered off, washed with water, HCL, and again with water and lastly with alcohol, dried and dissolved in CS_2. About ten per cent was found to be insoluble. The CS_2 solution (colorless) was divided into two equal parts, one of which was precipitated by ligroin; the white substance obtained, was dried and called "Red" acetylated and hydrolyzed D.

Analysis for Iodine.

Weight substance	.1422 g.
Weight Ag I	.1928 g.
% I found	73.25
Calc. for $(C_6H_2I_2O)_{17}$?	73.82

Molecular Weights.

Solvent, ethylene dibromide.

Weight substance	.5062 g.
Weight solvent	50. g.
Δ	.022°
Molecular Weight	5427.

No quinoid oxygen.

Re-Oxidation.

The second half of the CS_2 solution (75 c.c.) was shaken with 30 grams $Pb O_2$ for half an hour, filtered and precipitated with ligroin. The resulting "Red" was reprecipitated from bromoform solution and dried at 100° and called regenerated "Red" E.

Analysis for Iodine.

Weight substance	.1335 g.	.1321 g.
Weight Ag I	.1827 g.	.1795 g.
% I found	73.93	73.42
Calculated for $(C_6 H_2 I_2 O)_n$		73.82

Molecular Weights

Solvent, Ethylene dibromide.

Weight substance	.5232 g.	1.0302 g.	.5258g.
Weight solvent	50. g.	50. g.	50. g.
Δ	.022°	.038°	.015°
Molecular weight	5510	6396	8464

Per Cent Quinoid Oxygen.

Weight substance	.631 g.
Temperature	31
Pressure	74.2 cm.
Evolved N_2	0.95 c.c.
% Quinoid O found	0.36

Absence of Crystalline Derivatives.

During all the work on the "Red" and its derivatives a close watch was kept for crystalline products; in no case was one found either as insoluble product or in the filtrates. This is mentioned here in view of the statement by Kammerer and Benzinger (1) that they repeatedly recrystallized the "Red" from CS_2 and also because it was hoped to get a crystalline derivative.

All of these products, when obtained from CS_2 etc. by evaporation appeared as brittle shining varnishes, which easily shattered to coarse powders somewhat resembling fine crystals on casual inspection.

When obtained by precipitation, they all appeared under the high power of the microscope as small globules of rather uniform size.

(1) Loc. Cit.

Analysis of Some "By-Products".

Analysis of Insoluble "Red" for Iodine.

Weight substance	.1101 g.
Weight Ag I	.1476 g.
% I found	72.43
Calculated for $(C_6H_2I_2O)_{17}$	73.82

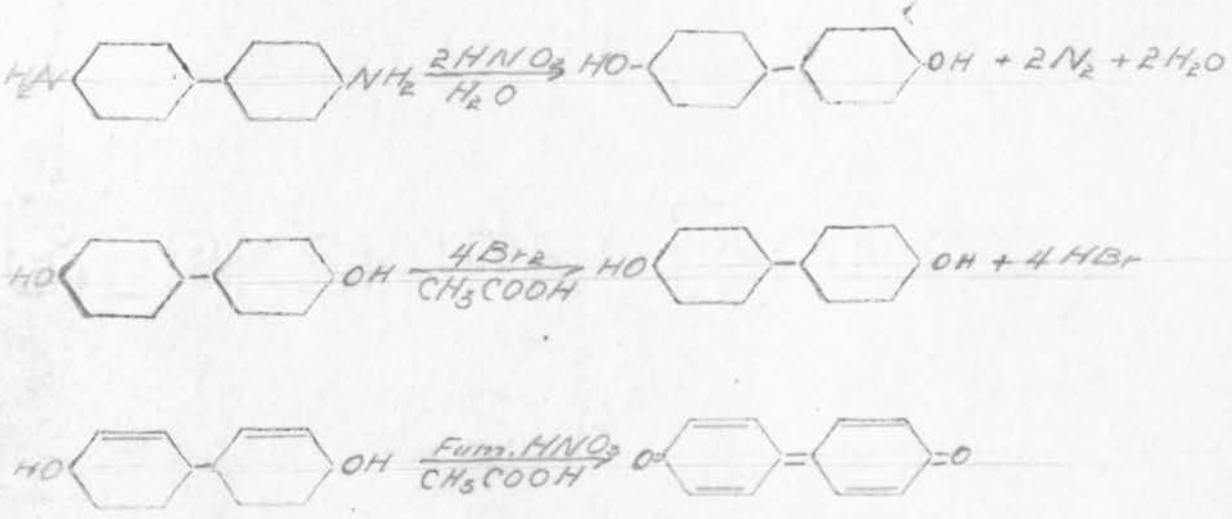
A sample of "Red" was obtained by evaporating the ligroin CS_2 filtrates in which several samples of "Red" had been precipitated. It was somewhat darker than the usual "Red".

Determination of Quinoid Oxygen.

Weight substance	.2457 g.	
Temperature	32.°	
Pressure	73.8	cm.
Evolved N_2	0.4	c.c.
% Quinoid O found	0.39	

On the True Di-nuclear Quinones.

Tetra bromo-dipheno-quinone was prepared by the method of Magatti (1). The following reactions were involved:



P. p. diphenol was first prepared by a modification of the method of Hirsch (2).

Twenty-five grams of benzidine were ground up in a mortar with 45 c.c. concentrated HCL and allowed to stand fifteen minutes. This blue-gray mixture was transferred to a flask and made up to 500 c.c. with cooled water. The theoretical amount of sodium nitrite (18.5 grams) was dissolved in 100 c.c.of water and added to the benzidine hydrochloride until test showed an excess. This usually

(1). B. 13, 226, 1880.

(2). B. 22, 335, 1889.

occurred before the whole amount had been added. The diazotized mixture was poured slowly into 3½ liters of actively boiling water, containing 5 c.c. of concentrated H_2SO_4. The mixture was kept actively boiling by passing insteam, until frothing ceased and the dark precipitate had coagulated, leaving a clear colorless solution.

The precipitate was then filtered off, while hot, on a pleated filter and on cooling the filtrate p.p. diphenol crystallized out in minute white flakes. About 5 grams of pure product were obtained. Melting point, 270°.

Several preparations were made; crystallization from alcohol was found not to raise the melting point.

Tetra-bromo-diphenol. (1)

Three and four tenths grams diphenol were dissolved in 175 c.c. glacial acetic acid and 15.6 grams of bromine in 25 c.c. glacial acetic.

The bromine solution was added quite rapidly to the diphenol at ordinary temperature. The mixture was heated for an hour on the water bath, cooled and the precipitate of tetra-bromo-diphenol filtered off, was washed with glacial acetic and water and dried.

It was recrystallized from alcohol, from which it separated as a white powder of melting point 269°.

Analysis for Bromine.

Substance	.1089
Ag Br	.1637
% Br	63.96
Calculated for $(C_6H_2Br_2OH)_2$	63.73

(1). Magatti B. 13, 226 -(1880)

Tetra-bromo-dipheno-quinone.

Three and eight-tenths grams of tetra-bromo-diphenol, in 100 c.c. glacial acetic, were treated with 5 drops fuming HNO_3 and heated on the water bath about three quarters of an hour. The beautiful blue-red crystals were filtered off, boiled with chloroform for a few minutes and then with alcohol for a few minutes, filtered off and dried. The product consisted of microscopic lozenge shaped crystals, remarkably uniform in size, blue by reflected and red by transmitted light. Crystals in quantity had a sparkling silky appearance, and purple color. They did not melt up to 278°.

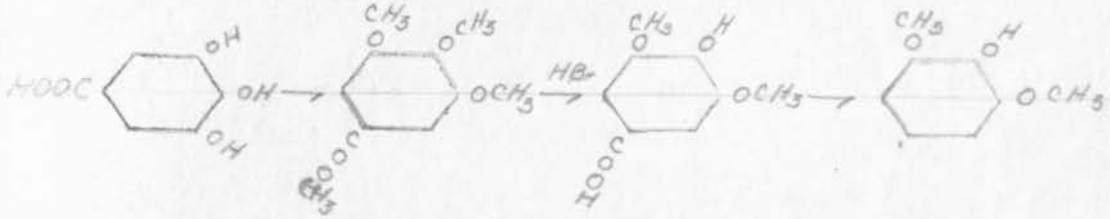
This quinone is very sparingly soluble in glacial acetic acid, chloroform and benzene. The solution is orange in color. The quinone separates from chloroform solution as needles, having the same color as the other variety.

Determination of Quinoid Oxygen.

Weight substance,	.5034	g.	.4700	g.
Temperature	32.°		32.°	
Pressure	73.8	cm.	73.8	cm.
Evolved N_2	13.8	c.c.	12.55	c.c.
% Quinoid O found	6.57		6.42	
% " " calculated for $(C_6H_2Br_2O)_2$			6.40	

Cedriret (1)

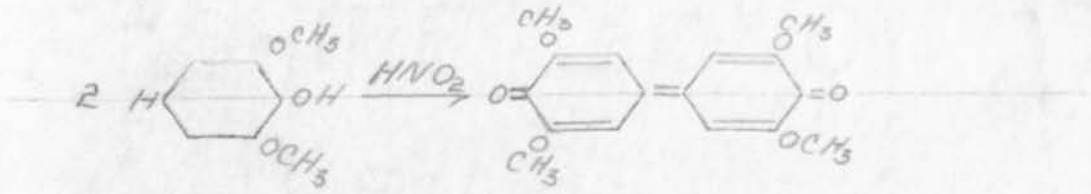
This was made by Graebe's directions from pyrogallol dimethyl ether. The ether was made by Mr. Remund according to the following reactions (Graebe):



About 2 grams of the ether dissolved in 2 c.c. glacial acetic acid and 20 c.c. water added. The calculated quantity of sodium nitrite was added, (.2 gram). The reaction took place immediately. NO_2 was given off and the Cedriret separated as glistening purple needles,, resembling Magatti's quinone very much. It was blue-red by reflected and red by transmitted light.

Both Cedriret and Magatti's quinone dissolve in concentrated sulphuric acid with a blue color, that from cedriret being more persistent.

The reaction:



(1). Graebe and Hess, Ann- 340,236. (1905)

Determination of Quinoid Oxygen.

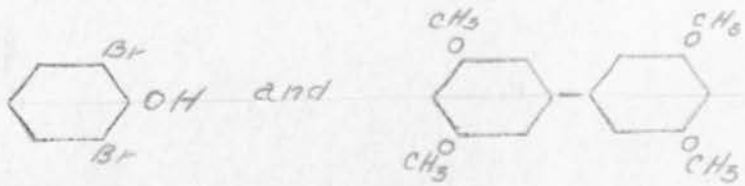
Weight substance	.1752	g.
Temperature	32.°	
Pressure	74.6	cm.
Evolved N_2	7.6	c.c.
% Quinoid O found.	10.57	
Calculated for $[C_6H_2(OCH_3)_2O]_2$	10.53	

Attempts to Prepare Adsorbtion Compounds.

Magatt[1]'s quinone in chloroform and in glacial acetic acid and in mixtures of both was boiled with the white amorphous dibromo-poly-phenylene oxide and the products separated both by precipitation (by alcohol) and by evaporating off the solvent.

In no case was any tendency noticed for the two to separate together as an adsorbtion compound. Each compound could be identified in the product without the aid of the microscope and the substance resulting had no resemblance to the Lautemann's Red or the orange substance obtained from tri-bromo-phenol salts. The two components were easily separated again by solution of the white oxide which is much the more soluble in benzene and $CH\ Cl_3$.

The compounds



on oxidation in water with HNO_2, or in Benzene or CS_2 with, $Pb\ O_2$, $Mn\ O_2$, or Ag_2O, do not give a di-nuclear quinone. The behavior of 2:6 di-bromo-phenol is given below.

White Halogenated Polyphenylene Oxides by Oxidation.

From Tri-bromo-phenol.

Four grams tri-bromo-phenol and 20 grams PbO_2 were shaken together in 50 c.c. CS_2 for about fifteen minutes.

The solution, (yellow), was filtered off and precipitated with ligroin, giving a white floculent precipitate. This was filtered off, washed with ligroin, redissolved in chloroform, precipitated with alcohol and finally dried at 100°; two grams were obtained. It was analyzed for bromine.

Substance	.1225 g.
Ag Br.	.1831 g.
% Br	63.61
Calculated for $(C_6H_2Br_2O)_n$	64.00

This product had every appearance of the polydibromophenylene oxides described in previous papers. (1)

From Tri-iodo-phenol.

Tri-iodo-phenol was treated in the same way. The product, a white amorphous substance, was purified by solution in bromoform and precipitated by alcohol and dried at 100°. Analysis:

Substance	.1509 g.	.1157 g.
Ag I	.2046 g.	.1560 g.
% I	73.26	72.85
Calculated for $(C_6H_2I_2O)_n$		73.82

This had the same appearance and solubilities as the white product obtained from the silver salt of tri-iodo-phenol. (1). It could not be oxidized to a colored compound by CS_2 and Pb O_2.

From 2:6 Di-bromo-phenol.

Four tenths of a gram of this phenol was dissolved in 5 c.c. CS_2 and shaken with 1 gram Pb O_2. The product was precipitated by ligroin and purified by solution in chloroform and precipitation by alcohol.

This product was similar to the other white amorphous compounds, though closer in solubility to the brominated ones than to those containing iodine. .15 grams of the purified oxide were obtained and analyzed for bromine.

Substance	.1018 g.
Ag Br	.1173 g.
% Br	49.04
Calculated for $(C_6H_2Br_2O)_n$	64.
" " $(C_6H_3BrO)_n$	46.78

Analysis of a similar product obtained by thermial decomposition of the silver salt of 2:6 di-bromo-phenol gave 53.94% and 53.68% Br.

From Para-bromo-phenol.

Para-bromo-phenol in CS_2 gives a white amorphous compound when treated with Pb O_2 which is similar to those already described. This product was not analyzed.

From Ordinary Phenol.

Twenty grams of ordinary phenol were dissolved in 75 c.c. benzene and 40 grams of PbO_2 were added. The mixture boiled spontaneously for a few minutes. After about half an hour the benzene was filtered off and the filtrate examined for a white amorphous compound, similar to those from halogenated phenols. About one gram of such a compound was found. It was precipitated by ligroin, was slightly yellow, and somewhat more soluble than the others, but completely amorphous. Four grams of unchanged phenol were extracted from the filtrate from this precipitation.

The amorphous compound was not analyzed.

Tri-bromo-phenol Bromide. (1)

(Tri-bromo-phenyl hypobromite) (2)

(Tetra-bromo-cyclohex a diene-one) (3)

A more rapid method than that outlined by Benedikt (4) was used.

Ten grams tri-bromo-phenol, melting point 93°, were dissolved in 300 c.c. water by addition of minimum amount of sodium hydroxide. After complete solution, the whole of the tri-bromo-phenol was precipitated by acetic acid solution, to get the phenol in a fine state of subdivision. This mixture was poured immediately into the bromine solution which had already been prepared as follows: 5 c.c. bromine dissolved in 2 liters of water in a three liter G. S. bottle, containing enough K Br to permit of easy solution of the bromine.

After addition of the tri-bromo-phenol, the bottle was stoppered and shaken on a shaking device for one hour. By that time, the tri-bromo-phenol bromide had usually collected in the bottom of the container in greasy looking yellow granules. These were filtered off rapidly on a pleated filter in a good draft. The granules of tri-bromo-phenol-bromide were allowed to drain for a few minutes and transferred to a small Büchner funnel and

(1) Benedikt Ann. 199, 128 (1879)

(2) Messenger and Vortmann B. 23, 2753 (1890)

(3) Thiele and Eichwede B. 33, 673, (1900)

(4) Loc. Cit.

sucked as dry as possible in two or three minutes.

The whole product was then dissolved in the minimum quantity of boiling chloroform, about 15-20 c.c., this being usually done on the water bath. The moisture was removed by filtering through a dry filter and the solution of tri-bromo-phenol-bromide evaporated and cooled by placing in a vacuum dessicator, attached to a filter pump. When about half the solution had evaporated, the yellow crystals were filtered off on a small Büchner funnel (a Gooch crucible) washed with ligroin and dried by spreading out on filter paper. Short yellow needles are obtained by this method, much resembling mono-clinic sulphur. By slower evaporation, the product can be obtained as larger polyhedrons.

The melting point of the needles is 115°-118°.

The success of the process seems to depend on having the phenol first in a very fine state of subdivision and in minimizing the time that the product is kept in contact with water without an excess of bromine being present and in keeping the water cool, (below 20°).

Less than two hours is necessary to get the first crop of crystals in this way; three crops were usually taken.

Benedikt's Hexabromo-dipheno-quinone.

This was first described by Benedikt (1) in 1879 and later prepared by others, viz. Oliver (2), Kastle (3), who corroborate Benedikt's observations. The substance as made by us, according to Benedikt's directions, also agrees with their description.

The pure tri-bromo-phenol bromide was heated in a current of dry CO_2 between 130° and 140°. Bromine vapor was given off freely; the residue, after the evolution of bromine had stopped, appeared as a transparent orange colored varnish.

This after solution in chloroform or benzene and precipitation with alcohol or ligroin appeared as the white flocculent precipitate, characteristic of all the white amorphous oxides so far described but possessing one marked difference, i.e. its easy solubility in ether. It is precipitated from ether solution as the usual white flocks.

Concordant analyses by the other authors show the substance to contain three atoms of bromine per benzene ring. Our product was not analyzed.

This substance could not be oxidized to a colored compound by CS_2 and $Pb\ O_2$ as were reduction products of the colored amorphous compounds.

(1) Ann. 199, 128, (1879)

(2) R d.t. ch., 28, 358, (1909)

(3) J. A. C. 27, 16 ( )

Molecular weights by Olivier (1) give 2000 cryoscopically in benzene and 2500 ebullioscopically in chloroform.

Determination of the % quinoid oxygen, by hydrozine, gave negative results as shown by the following:

Substance	.562 g.
Temperature	29.
Pressure	745.
Evolved N_2O.	0.

(1) Loc. Cit.

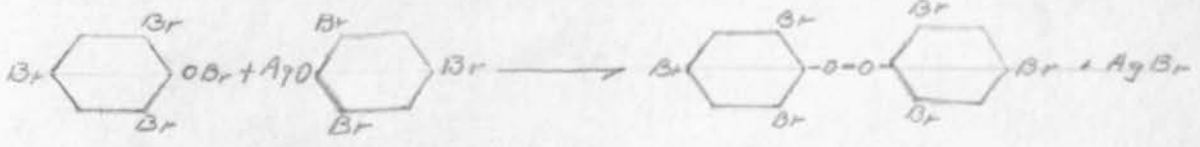
Action of Tri-bromo-phenol Bromide on the Silver Salt of Tri-bromo-phenol.

Kastle and Loevenhardt (1) claim to have obtained Benedikt's quinone by action of tri-bromo-phenol bromide on the silver salt of tri-bromo-phenol.

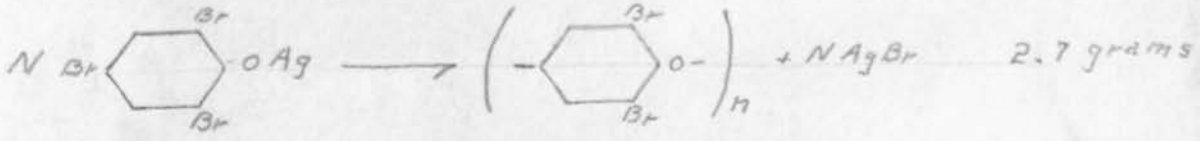
As we had reason to doubt this, the work was repeated.

Four and eight-tenths grams of tri-bromo-phenol bromide were dissolved in about 20 c.c. of chloroform to which 45 grams of the red silver salt of tri-bromo-phenol were rapidly added. A transient greenish blue color appeared as the red of the silver salt disappeared, the whole mixture becoming yellow in a very short time. The precipitated silver halide was filtered off and alcohol added to the filtrate. This caused the separation of a typical white amorphous substance which was filtered off, dried and weighed.

When dry, it was slightly yellow; 2.3 grams were obtained. Calculated from the equation:



6.7 grams. From the equation:



(1) Ann. 27, 31-52, 1902.

This was repeated, using 2 grams of the white silver salt and 1.83 grams tri-bromo-phenol bromide in 100 c.c. chloroform. The salt was added slowly with good shaking. The product was precipitated as before and was nearly white. The chloroform was boiled out of the alcoholic filtrate, whereupon an orange colored sticky substance separated. On adding water to the alcoholic liquid residue, separated from this sticky substance, a voluminous white crystalline precipitate appeared which caused the whole mass to gelatinize and, on drying without purification, melted at 80°.

This substance, dissolved in N/5 KOH, gave the red precipitate on adding Ag NO_3 solution, characteristic of tri-bromo-phenol.

In another trial, 4.10 grams of fresh tri-bromo-phenol bromide were dissolved in 75 c.c. chloroform; 4.38 grams of red tri-bromo-phenol silver salt were mixed with 15 c.c. chloroform and the two mixed in the dark. After standing in the dark for about 15 minutes, the mixture was brought out; the amorphous compound separated in the usual way, also the sticky orange-red substance, and the crystallizing product precipitated as above by water, purified by several re-solutions in alcohol and precipitations by water, was dried and found to melt at 91.5°. Melting point of tri-bromo-phenol is 92-93°.

The white amorphous substance was purified by precipitation from chloroform solution by alcohol, dried at 100 and analyzed for bromine.

Substance	.1071 g.	.1028 g.
Ag Br	.1593 g.	.1546 g.
% Br	63.30	64.00 ?
Calculated for $(C_6H_2Br_2O)_{17}$	64	
" " $(C_6H_2Br_3O)_{17}$	72.7	

In order to determine the amount of unchanged tri-bromo-phenol bromide present at the end of the reaction it was titrated with N/20 sodium thiosulphate, after the addition of KI, water and sulphuric acid.

Olivier (1) found tri-bromo-phenol bromide and potassium iodide in water to react according to the following equation:

$$C_6H_2Br_3O\,Br + 2\,KI \longrightarrow C_6H_2Br_3OK + K\,Br + 2\,I$$

Standardization of N/20 $Na_2S_2O_3$.

.3000 grams of fresh tri-bromo-phenol bromide were used, dissolved in 25 c.c. chloroform which had been purified by shaking once with N/5 KOH and three times with water. To this solution was added 25 c.c. water and 5 c.c. 20 % KI solution, and the whole made faintly acid with dilute sulphuric acid, 1-2 c.c.

The thiosulphate solution was run in and after each addition, the flask was stoppered and shaken violently. The end point was taken just before the iodine color disappeared from the chloroform layer.

	T.B.P.B.	$Na_2S_2O_3$	T.B.P.B./c.c.$Na_2S_2O_3$
I.	.3000 g.	24.8 c.c.	.0121
II.	.3000 g.	25.7 c.c.	.0117
III.	.3000 g.	25.9 c.c.	.0116
Av.		25.5 c.c.	.0118

Titration of Reaction Mixture.

Four and ten-hundredths grams of tri-bromo-phenol bromide were dissolved in 25 c.c. purified chloroform and poured into .438 grams of silver salt (white) previously mixed with 5 c.c. of chloroform. This was carried out in the dark and after about fifteen minutes, brought out and titrated exactly as in the standerdization.

		c.c.	Unchanged	%	% Unaccounted for.
S'pl.	T.B.P.B.	$Na_2S_2O_3$	T.B.P.B.		
I.	.410	24.3	.2867	69.8	30.2
II.	.410	24.1	.2844	69.3	30.7

Tri-bromo-phenol Bromide in Sunlight.

A sample of tri-bromo-phenol bromide in CS_2 was exposed to sunlight for two days, the solution gradually becoming a deep orange red. The white amorphous substance was separated by ligroin, purified by a second precipitation and analyzed for bromine.

Substance	.1033 grams	
Ag Br	.1587 "	
% Br.	65.38	
Calculated for $(C_6H_2Br_2O)_n$		64.00

Tri-bromo-phenol Bromide and Mercury.

Three grams of tri-bromo-phenol bromide were dissolved in 25 c.c. benzene and were sealed up with about 2 c.c. of benzene, very little air being included. The mixture was shaken rapidly for three quarters of an hour then opened and filtered. The filtrate was slightly yellow and on addition of alcohol, gave a white flocculent precipitate, which on drying, weighed half a gram. This was reprecipitated, dried at 90°-100° and analyzed for bromine.

Weight substance	.1061	.1097
Weight Ag Br.	.1589	.1639
% Br. found	63.73	63.58
Calculated for $(C_6H_2Br_2O)_n$		64.00

Besides the excess of mercury, a white insoluble powder was left from the first filtration. This was extracted with chloroform and a small amount of white amorphous substance obtained. In neither of the white precipitates from benzene solution by alcohol could mercury be detected.

Another sample of 5 grams of tri-bromo-phenol bromide in 125 c.c. benzene was shaken with 5 c.c. mercury for one hour. This gave one gram of white oxide.

One gram of tri-bromo-phenol bromide was shaken with 15 c.c. benzene and 2 c.c. Hg occasionally for three days. This yielded .3 gram of the white oxide.

Tri-chloro-phenol Bromide.

This has been described by Kastle (1) and was made by us in essentially the same way as the tri-bromo-phenol bromide already described.

Ten grams of pure tri-chloro-phenol were dissolved in 300 c.c. water and the minimum amount of alkali. This solution was made distinctly acid by acetic acid just previous to putting it into 1500 c.c. of bromine water containing 5 c.c. bromine and 5 grams of KBr. The whole, in a glass stoppered bottle was shaken for one hour on a shaking device. It was removed and filtered as rapidly as possible on a pleated filter, the product being transferred to a Büchner filter for a few minutes. At this stage it appeared as greasy yellow nodules; these were dissolved in the minimum quantity of hot chloroform on the water bath, the water etc. removed either by filtering through a dry filter or skimming with a piece of damp filter paper. The solution was allowed to crystallize in vacuo, the first crop being taken when the chloroform had about half evaporated. This was filtered off in a Gooch crucible used as a Büchner funnel, washed with ligroin and dried on filter paper in the air. The product was lemon yellow needles, melting point 108°-109°. The tri-chloro-phenol bromide is considerably more soluble in chloroform than the tri-bromo-phenol bromide; otherwise they are very much alike.

(1) Loc. Cit.

Effect of Heating in CO_2.

A sample of the tri-chloro-phenol bromide was heated to 130°-140° in a current of CO_2 dried by passing through concentrated sulphuric acid and over calcium chloride. The loss in weight was noted.

Weight of flask and tri-chloro-phenol bromide	20.6193 g.
" " "	17.3678 g.
" " ..... " " " "	3.2515 g.
" " " etc. after heating.....	19.9664 g.
Loss	.6529 g.
% Loss	20.08

The evolved bromine was bubbled through a mixture of silver nitrate, sodium nitrite and sufficient nitric acid to redissolve the precipitate first formed. The resulting silver halides were reduced with zinc and sulphuric acid and the solution tested for chlorine by boiling out the bromine freed by addition of small quantities of potassium persulphate. The solution, after all the bromine was gone, gave a white precipitate with silver nitrate.

The yellow varnish like residue from the tri-chloro-phenol bromide was worked up in the usual way and after precipitation by alcohol from chloroform solution, was analyzed for halogen.

Weight substance	.1058 g.
Weight Ag Cl(Br)	.2156 g.
% Cl found	50.38
Calculated for $(C_6H_2Cl_3O)_7$	57.06

Another sample was precipitated from ether solution by alcohol twice dried and analyzed.

Weight substance	.1050
Weight Ag Cl (Br)	.2152
% Cl found	50.68
Calculated for $(C_6H_2Cl_3O)$	57.06

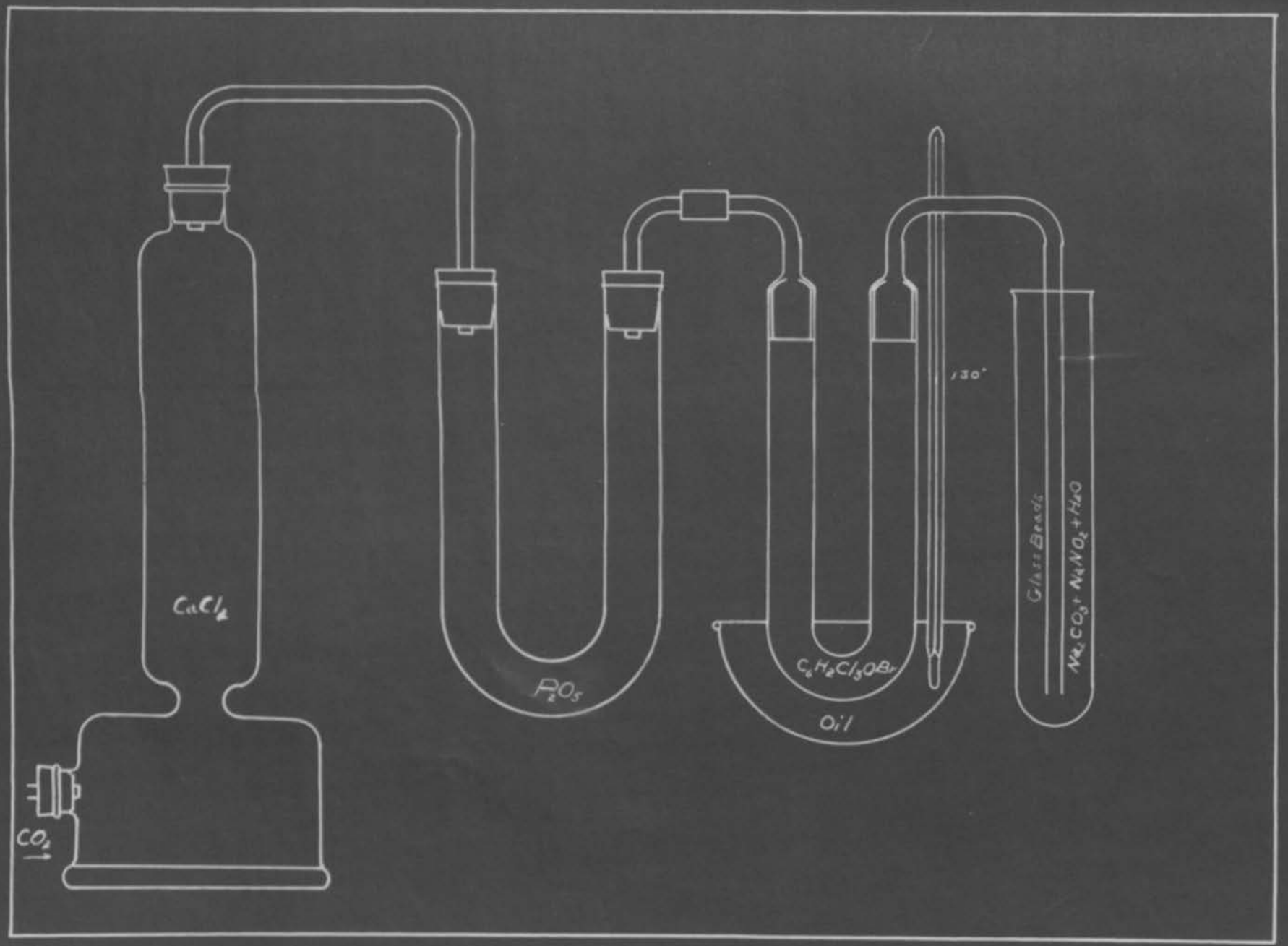
In a repitition of this experiment, the evolved bromine was caught in 100 c.c. of water containing 2 grams of Ag NO_3 and about one gram of Na NO_2 and just enough nitric acid to clear.

The precipitated silver halide was filtered off and weighed. The amorphous residue was not weighed.

	I.	II.
Weight tri-chloro-phenol bromide....	1.0000 g.	1.0000 g.
Crucible and Ag halide.....	12.4247 g.	12.8352
Crucible.....	12.0030	12.4247
Silver halide.....	.4217	.4105

The experiment was repeated using a Liebig absorbtion bulb containing potassium iodide solution to absorb the bromine with the following results.

	I.	II.
Weight of flask and T.Cl.P.B.....	18.6962	19.7952
" " ".....	17.3617	18.4386


CuCl2
CO2
P2O5
C6H2Cl3OBr
Oil
130°
Glass Beads
Na2CO3+NaNO2+H2O

	I.	II.
Weight T.Cl.P.B.	1.3345	1.3566
" after heating	18.4386	19.5246
Loss	.2576	.2706
% Loss	19.30	19.95
Wt. absorbtion apparatus Br (Cl)	61.1882	61.4375
" " "	60.9587	61.1882
Gain	.2295	.2493
% Gain	17.18	18.38

This method with further modifications was used for more determinations. The apparatus used is shown in the drawing (page 97)

Carbon dioxide was generated from sulphuric acid and sodium bicarbonate, passed through a calcium chloride tower and then through a U tube containing phosphorus pentoxide. It was then passed through the U tube containing the tri-chloro-phenol bromide (this being fitted with ground glass stoppers) and finally bubbled through the absorbing solution in the large test tube fitted with glass beads. The absorbing solution consisted of 50 c.c. of water containing 2 grams of sodium nitrite and 2 grams of sodium carbonate.

The U tube was weighed before and after charging with tri-chloro-phenol bromide, then placed in the train of apparatus and heated to 130°-140° in an oil bath. The bromine came off rather suddenly.

After the reaction was over, the U tube was cool-

ed and weighed again. The absorbing liquid was filtered off from the beads which were washed and the washings added. The combined solutions were acidified with nitric acid, the halogen precipitated by silver nitrate and weighed.

The silver halides were reduced with zinc and sulphuric acid and the bromine driven out of the reduction product by boiling after addition of KSO_4 until starch-potassium iodide paper held over the boiling solution gave no further indication of bromine.

This solution was cooled diluted and the chlorine precipitated by silver nitrate, filtered off and weighed.

	I.	II.	III.
Wt. U tube T.Cl.P.Br.....	19.5255	19.6230	19.4133
" " "	18.5455	18.5450	18.5450
" T.Cl.P.Br.....	.9800	1.0780	.8683
" U tube after heating..	19.3596	19.4218	
Loss	.1659	.2012	
% Loss.....	16.93	18.67	
Wt. Silver halide	.4032		.3730
Wt. Silver chloride.....	.0508		.0583
Wt. Silver Bromide by (diff)	.3524		.3147

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The Silver Salt of Triiodophenol and its Catalytic Decompositions

By G. H. Woollett

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE SILVER SALT OF TRIIODOPHENOL AND ITS CATALYTIC DECOMPOSITIONS.

BY G. H. WOOLLETT.

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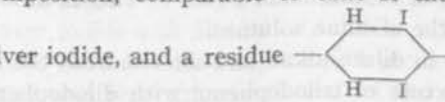
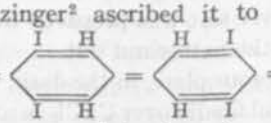
In the course of further study of the catalytic decomposition of silver salts described by Hunter,[1] *et al.*, it became necessary to investigate the

[1] THIS JOURNAL, 38, 1761 (1916).

behavior of the silver salt of triiodophenol. On account of its symmetrical nature, it was expected that this salt would give a smooth catalytic decomposition, comparable to that of the salt of tribromophenol, giving silver iodide, and a residue  which should then polymerize as did those already studied. Further, the result of this polymerization could not fail to be of interest, in comparison with the colored compound, of like empirical composition, already studied by several chemists, and now known as tetraiododiphenylenequinone.

This had been originally obtained by the action of iodine and sodium carbonate on phenol, by Lautemann[1] who believed it to be an aromatic oxide and called it diiodophenylene oxide. Kammerer and Benzinger[2] ascribed it to the formula of a tetraiododiphenoquinone,  and this formula has since been retained. It is proposed to show in a later communication that this formula also is erroneous.

On making very pure samples of the silver salt, it was discovered that it was possible to obtain from it at will either a white amorphous product exactly like those described in the paper already cited, or a red substance, which was easily shown to be identical with Lautemann's red substance.

The present preliminary paper will contain a description of the properties of the silver salt, and of the conditions under which each of the above transformations occurs.

The Silver Salt of Triiodophenol.—The phenol was made by the following method, which is based on that of Körner:[3] One-fifth gram molecule of phenol and the amounts of iodine and iodic acid required by the equation

$$5C_6H_5OH + 6I_2 + 3HIO_3 = 5C_6H_2I_3OH + 3H_2O$$

were each dissolved separately in a slight excess of 2 N potassium hydroxide solution. The three solutions were then mixed in a three-liter bottle with glass stopper, and diluted to two liters. To the solution dilute hydrochloric acid was slowly added, with good stirring. Iodine was liberated and at first very rapidly taken up, with formation of a white precipitate. After a while the color of free iodine remained for several minutes at a time. When this point was reached, the reaction mixture was rapidly made distinctly acid and placed on the shaking machine for two hours. The precipitate was then chiefly triiodophenol, colored with iodine, giv-

[1] *Ann.*, **120**, 309 (1861).
[2] *Ber.*, **11**, 557 (1878).
[3] *Ann.*, **137**, 214 (1878).

ing it a brown color. Dilute bisulfite solution was now added till the iodine color disappeared, and the precipitate was filtered off. It was a light pink, owing to the presence of a little of "Lautemann's red." This is formed by the action of free iodine on the alkaline solution.

The precipitate was dissolved in dilute alkali and filtered from the insoluble red substance. The mixture of triiodophenol with diiodophenol was reprecipitated from the filtrate by acetic acid, filtered, and washed. It was again dissolved in dilute alkali, treated with bone black without heating, and reprecipitated. It weighed about 80 g. It was purified by repeated solution in about 1500 cc. of alcohol and addition of an equal amount of water, until it gave the proper melting point, 156°. Less careful treatment yielded only products of much lower melting points. Our phenol agreed in every respect with the description of Körner.

From this very pure phenol a sample of silver salt was prepared in the usual way by precipitation from a solution of the potassium salt.

It was washed very carefully, dried on a porous plate, in the dark, then at 70° in a drying oven for nearly an hour, and finally over $CaCl_2$ *in vacuo*. The sample was a full lemon yellow, with no appearance of change at any time during the procedure. It was analyzed for both silver and iodine by the method of Carius.

For Ag, subst., 0.1831 g., AgI 0.0737 g.; for I, subst., 0.1114 g.; AgI, 0.1355 g.
Calc. for $C_6H_2I_3OAg$: Ag, 18.65%; I, 65.82%. Found: Ag, 18.55; I, 65.72.

Since this salt is described by Hantzsch[1] as white in color, several attempts were made to obtain a colorless variety, without success. To see if the color might be due to an impurity, a sample of yellow salt was reduced by zinc and sulfuric acid, and the phenol so obtained was used to make another sample of silver salt, which was again yellow. On acidification of an ammoniacal solution, the yellow salt reappeared. Finally, silver nitrate was added to a glacial acetic acid solution of triodophenol, when a yellow precipitate fell, which was collected, washed, and analyzed. It was low in silver, as was to be expected from its method of manufacture.

Subst., 0.1580 g., AgI, 0.0587 g. Calc.: Ag, 18.65. Found: Ag, 17.08.

Formation of the White Oxide from the Silver Salt.—On treating the silver salt with cold ethyl iodide, most of it was converted into the normal ether triiodophenetole. However, the formation of a small amount of amorphous substance could be demonstrated. If the tendency of the silver salt to decompose was increased by heating, the desired catalytic decomposition occurred, as in the following experiment:

Three grams of good silver salt, in small lumps and powder, were heated about five minutes on the water bath, in an Erlenmeyer flask. Ten cc. of cold ethyl iodide were then poured on the salt. A vigorous reaction at

[1] *Ber.*, 40, 4875 (1905).

once resulted, in every respect analogous to those observed with the salt of tribromophenol and other phenols, except that the color was grass green instead of blue. The color lasted for about fifteen minutes. The silver iodide was filtered off, and on addition of ethyl alcohol to the filtrate, there resulted a slightly pink precipitate. A single solution in bromoform and reprecipitation removed the color, giving a white, amorphous powder, of properties similar to those of the polydibromophenylene oxide of Hunter, except for a less degree of solubility—for instance, it is almost insoluble in chloroform. It was carefully dried and analyzed.

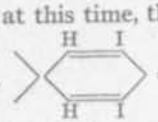
Calc. for $(C_6H_3I_2O)_x$: I, 73.82%. Found: I, 73.60, 73.80. Carius subst., 0.1394, 0.1063; AgI, 0.1902, 0.1452.

If both the salt and the ethyl iodide were heated before mixing, the action was very vigorous indeed, but gave the same white oxide. The pink color in the crude oxide was apparently due to the formation of a small amount of "Lautemann's red."

"Lautemann's Red" from the Silver Salt.—It was noticed that on long exposure to sunlight, the silver salt became red, suggesting the possibility of a second type of decomposition. Comparison with Lautemann's[1] method of making the red substance led to its preparation in the following manner:

A sample of the silver salt was ground up and suspended in water, and then treated with a single drop of a solution of iodine in potassium iodide. As the mixture was shaken, the silver salt became a dark purple in color, the solution still seeming to contain iodine. The colored solid residue was filtered off, dried, and extracted with carbon bisulfide. From this ligroin precipitated a dark red substance, entirely amorphous, and agreeing in every respect with samples made by the method of Lautemann. It was washed with alcohol, dried, and analyzed.

Subst., 0.1078; AgI, 0.1462. Calc. for $(C_6H_3I_2O)_x$: I, 73.82%. Found: 73.28.

That this formation of Lautemann's red instead of white amorphous substance is not due simply to the presence of iodine was easily shown by suspending dry salt in benzene, and adding a slight amount of iodine. This led to a formation of a white amorphous solid, only faintly tinged with pink, showing that iodine can also cause the formation of the white oxide. The question of the relation between the white and the red polymers of the unsaturated residues is being studied in this laboratory. It is perhaps worth pointing out, at this time, the possibility of a quinoid form of the unsaturated residue,  = O although any effect that could be due to such a form, could also result by a simple shifting of val-

[1] *Loc. cit.*

ences without atomic rearrangement, after polymerization of the benzenoid form.

Summary.

The silver salt of triiodophenol has been prepared in a very pure state, but the colorless form described by Hantzsch has not been obtained, all the samples found being yellow.

This salt, when warmed, gives with ethyl iodide a reaction exactly like that shown by the silver salt of tribromophenol, yielding silver iodide and an unsaturated residue which polymerizes to a white oxide.

$C_6H_2I_3OAg = AgI + (—C_6H_2I_2O—)$

$n(—C_6H_2I_2O—) = (C_6H_2I_2O)_n$, white amorphous.

The salt, when treated with a very little iodine in water, gives instead of the white oxide, the red substance first described by Lautemann.

$C_6H_2I_3OAg = AgI + (—C_6H_2I_2O—)_n(— C_6H_2I_2O—) =$

$(C_6H_2I_2O)_n$, red amorphous.

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